

Monday Morning, October 28, 2013

Energy Frontiers Focus Topic

Room: 101 A - Session EN+PS+TF-MoM

Thin Film, Organic, and Chalcogenide Solar Cells

Moderator: Y. Xu, Oak Ridge National Laboratory

8:20am EN+PS+TF-MoM1 Understanding (?) Solar Devices through Soft X-Ray and Electron Spectroscopy, C. Heske, UNLV and KIT

INVITED

The purpose of this talk is to demonstrate how a tool chest of soft x-ray and electron spectroscopies (in particular using high-brilliance synchrotron radiation) is uniquely suited to unravel the electronic and chemical properties of surfaces and interfaces in thin film solar cells. We will show how photoelectron spectroscopy (PES), Auger electron spectroscopy (AES), inverse photoemission (IPES), x-ray emission spectroscopy (XES), and x-ray absorption spectroscopy (XAS) can be suitably combined to derive band gaps, study local chemical bonding and electronic level alignment, and derive insights into chemical stability at surfaces and interfaces. As examples, Cu(In,Ga)(S,Se)₂ and CdTe thin films and devices will be discussed.

9:20am EN+PS+TF-MoM4 Continuous-Flow Chemical Bath Deposition of Zn_xCd_{1-x}S Thin Films For Chalcopyrite Solar Cells, B.S. Tosun, J.T. Abrahamson, A.A. Gunawan, K.A. Mkhoyan, S.A. Campbell, E.S. Aydil, University of Minnesota

Kesterite and chalcopyrite thin film solar cells have an n-type metal sulfide (e.g., CdS, ZnS or Zn_xCd_{1-x}S) buffer layer deposited on the p-type absorber. This buffer layer is typically grown using chemical bath deposition (CBD) from metal salts and thiourea in basic aqueous solutions. In a typical CBD system, the entire solution, including the substrate, is heated. This leads to homogeneous nucleation of the metal sulfide particles in addition to the heterogeneous reaction that deposits the desired buffer layer on the substrate. This homogeneous nucleation and growth of particles wastes chemicals and causes problems with solar cells when the particles stick on the absorber surface. To solve these problems we have developed a continuous chemical bath deposition (CF-CBD) system that allows the deposition of Zn_xCd_{1-x}S films on 4-inch diameter substrates at temperatures ranging from 50 to 85 °C without significant solution temperature rise and without homogeneous nucleation and growth. Only the substrate is heated to the deposition temperature while the CBD solution is rapidly circulated between the bath and a chilled reservoir. The key features of the design are easily scalable and adaptable to roll-to-roll deposition. We have demonstrated that the CF-CBD system can be used to deposit uniform thickness and composition Zn_xCd_{1-x}S films across 4-inch diameter substrates for a variety of x values by changing the concentrations of the Zn and Cd salts in the bath. Addition of ethylenediaminetetraacetic acid disodium to the chemical bath deposition is the key to preventing deposition on surfaces other than the heated substrate surface and key to obtaining films with uniform composition and structure across the film's thickness. Films were characterized using x-ray diffraction, Auger depth profiling, spectroscopic ellipsometry, transmission electron microscopy and Kelvin probe force microscopy. The effect of deposition parameters such as temperature, bath stirring rate and bath composition on the structure and composition of the films will be discussed.

9:40am EN+PS+TF-MoM5 Development of Plasma-Enhanced Vapor Transport Deposition of CdTe Absorbers, J. Beach, C.A. Wolden, J.J. Li, Colorado School of Mines

Development of plasma-enhanced vapor transport deposition of CdTe absorbers

Jiaojiao Li, Joseph Beach, and Colin A Wolden

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Cadmium telluride is a leading absorber material for thin-film solar cells. However, state-of-the-art open circuit voltages (V_{oc}) of CdTe thin film solar cells fall ~350 mV below the value expected based on the band gap of CdTe. V_{oc} is mainly compromised by the structural defects, low carrier density and low recombination lifetime. Conventional methods to eliminate defects require the use of high temperature deposition or annealing processes which are incompatible with low cost soda-lime glass. The low hole density is because CdTe is difficult to dope due to numerous self-compensation mechanisms. CdCl₂ treatment is always used to passivate the grain boundaries and increase carrier lifetime, but additional Cd may induce Te vacancies. In this work we introduce plasma-enhanced vapor transport deposition (PEVTD) as an alternative technique for thin film CdTe

synthesis. The viability of vapor transport deposition (VTD) is demonstrated by First Solar's use of this approach to produce both the lowest cost modules. Plasma deposition techniques are able to introduce energy to films at low thermal budget. PEVTD is a hybrid of these two technologies, and we expect it to also be amenable to scale-up. In this method, high energy electrons dissociate Te₂ dimers into reactive Te species, so a high quality Te rich film may be achieved at low temperature. Moreover, plasma enhancement may activate group V dopants to dope CdTe at a higher concentration. Finally, active gases such as H₂S or SO₂ are added to the carrier gas stream to passivate interface defects and increase minority carrier lifetime. In this talk we discuss the design, construction, and operation of this reactor. We describe the dependence of the CdTe film quality on the kind of gases we use, plasma power, and substrate temperature. Films are characterized using XRD, SEM, UV-Vis-NIR spectrophotometry, Hall and light and dark current-voltage measurements.

10:00am EN+PS+TF-MoM6 Self-Limiting Growth of Pyrite Solar Absorbers using Pulsed PECVD, C. Sentman, Colorado School of Mines, M. O'Brien, Trinity College Dublin, Ireland, C.A. Wolden, Colorado School of Mines

Pyrite, FeS₂, is a non-toxic, earth abundant semiconductor that offers several potential advantages as a photovoltaic material, including low cost, large absorption coefficients and a band gap that is suitable for the harnessing of solar energy. Conventional thin film deposition techniques typically require the use of a post-deposition annealing step in elemental sulfur in order to achieve stoichiometric material. This cumbersome step is usually conducted in sealed quartz ampoule, requiring precise control over sulfur mass, time, and temperature. In this talk we introduce pulsed plasma-enhanced chemical vapor deposition (PECVD) as an alternative technique for thin film pyrite synthesis. In pulsed PECVD a mixture of iron pentacarbonyl (IPC, Fe(CO)₅) diluted in H₂S is delivered continuously to the reactor while the plasma is pulsed using square wave modulation at low frequency (~1 Hz). The concept is that IPC absorbs during the plasma off step, and that it is fully sulfurized *in situ* during the plasma on step. The process offers digital control over thickness with control on the order of ~1 Å/pulse. In this work we demonstrate the conditions required to achieve self-limiting growth of pyrite thin films. The dependence of pyrite deposition rate and material quality as a function of relevant variables such as H₂S:IPC ratio, plasma duty cycle, plasma power, pressure and substrate temperature is described. Films are characterized using a suite of analytical techniques including Raman, XRD, FESEM, and UV-Vis-NIR spectrophotometry. Through appropriate control of deposition parameters stoichiometric FeS₂ could be deposited at controllable rates between 0.1 – 1 Å/pulse without the need for post-deposition annealing. The onset of thermal CVD between these precursors was found to be ~300 °C, and it is shown that this process leads to the formation of undesirable sulfur-deficient phases. Processing could also be used to tune the pyrite to marcasite ratio. Films display expected absorption coefficient (~10⁵ cm⁻¹) and optical band gap (~1 eV). We are currently analyzing their optoelectronic properties and will report on the process-structure-property relationships in this system.

10:40am EN+PS+TF-MoM8 Surface Energetics of AgInSe₂ Thin Films, P. Peña Martin, A. Rockett, University of Illinois at Urbana Champaign

The chalcopyrite system has contributed the top performing absorber layer for thin film photovoltaic devices, Cu(In,Ga)Se₂, but the surface properties of these compounds are not well understood. While CuInSe₂ (CIS) has proven difficult to obtain atomically resolved surface images, the AgInSe₂ (AIS) surface has been recently observed. Study of the surface structure, growth mechanics and defects of AIS can provide important details of its behavior, as well as yielding insight into other chalcopyrites, like CIS, by comparison of the results. This work presents the results of growing epitaxial AIS films and studying their surface morphology to help understand its growth behavior and to transfer this knowledge to help understand the growth of chalcopyrites in general.

Thin films of AIS were grown by hybrid sputtering and evaporation technique on (110), (110), (111), and (-1-1-1) GaAs substrates. Film thicknesses were around 500 nm, and the substrate temperature was varied from 500-700°C. Their microstructures were characterized by a variety of techniques including scanning electron (SEM), scanning tunneling (STM), and atomic force (AFM) microscopies, as well as x-ray diffraction (XRD). SEM shows that the films all exhibit facets or features that are aligned across the sample, indicating that the films are epitaxial, confirmed by x-ray diffraction.

AIS was found to show a similar preference as does CIS for polar facets. The films grown on GaAs (111) and (-1-1-1) are very smooth with

individual atomic steps resolvable, while growth on GaAs (110) results in films that spontaneously facet to two polar faces with roughnesses that differ dramatically. AFM line profiles indicate an angle of $\sim 68^\circ$ between the faces, as expected for the angle between polar (112) planes. One side of the facets is stepped, with triangular features pointed toward the "peak" of the facet. The other side shows fewer features, with occasional triangular terraces pointed toward the "valley" instead. This is consistent with a chemical difference between these two surfaces. The films grown on (100) GaAs are highly featured, with rectangular pits that are likely (111) terminated. The features on films grown on both (100) and (110) substrates both show smaller size than films grown on CIS, even with a higher homologous temperature for AIS.

11:00am **EN+PS+TF-MoM9 Microstructure Evolution During Annealing of Copper Zinc Tin Sulfide Colloidal Nanocrystal Coatings to form Large-Grain Polycrystalline Thin Films**, *B.D. Chernomordik, A.E. Bédard, D.D. Deng, A.A. Gunawan*, University of Minnesota, *D.J. Norris*, ETH Zürich, Switzerland, *E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, or CZTS), copper zinc tin selenide ($\text{Cu}_2\text{ZnSnSe}_4$, or CZTSe), and their alloys are candidates for environmentally sustainable light absorbing materials for thin film solar cells because they are composed of abundant elements. In one potentially low-cost approach to making solar cells, coatings drop-cast from colloidal dispersions of CZTS nanocrystals (NCs) (inks) are annealed to form 1-3 micron thick polycrystalline films with 1-3 micron grains. We synthesize CZTS NC inks using rapid thermal decomposition of copper, zinc, and tin diethyldithiocarbamate precursors in presence of hot (150-300 °C) oleylamine. The synthesis temperature determines the NC size, which can be tuned from 2 to 25 nm. The formation of CZTS is confirmed using X-ray diffraction (XRD), Raman spectroscopy, and energy dispersive X-ray spectroscopy (EDS). Following synthesis, the NCs are dispersed in toluene and NC films are cast on various substrates including quartz and soda lime glass. One micron or thicker films cast from <10 nm NCs crack due to capillary forces during drying. Cracks are reduced significantly when films are cast from 25 nm nanoparticles. The NC films are then placed in quartz tubes with pure S, Se, or a mixture of the two, evacuated to 10^{-6} Torr, sealed, and then heated for the desired times (1-8 hours) at the desired temperatures (500-800 °C). This annealing approach provides excellent and very reproducible control of the annealing temperature and S and/or Se pressure over the film. The resulting films are characterized using a suite of techniques, including XRD, electron microscopy, EDS, and Raman scattering. We have explored the extent to which vapor species, vapor pressure, substrate choice, carbon content in the NC film, annealing time, and annealing temperature affect the mechanisms by which the polycrystalline films form and how their microstructure evolves. Depending on the annealing conditions, the CZTS NCs sinter and grow to sizes ranging from a hundred nanometers to a few microns. In addition to sintering, we observe abnormal grain growth, which, if encouraged, can lead to formation of single-crystal CZTS grains up to 10 microns in size. Raman scattering spectra collected from these large CZTS crystals show that the crystals have texture, preferring two orientations. The surface energy difference between the NCs and the large grains is the driving force for abnormal grain growth, which appears to be enhanced at high temperatures but reduced significantly on SLG and at high S pressures. The abnormal grain growth can be turned on or off via control of these variables.

11:20am **EN+PS+TF-MoM10 Enhanced Grain Growth in $\text{Cu}_2\text{ZnSnS}_4$ Thin Films via Vapor Transport of Alkali Metal Impurities**, *M. Johnson**, University of Minnesota, *S. Baryshev*, Argonne National Laboratory, *E. Thimsen*, *M. Manno*, *X. Zhang*, *C. Leighton*, *E.S. Aydil*, University of Minnesota

While power conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) based solar cells have increased relatively rapidly, very little research has been focused on the effects of the substrate on CZTS films. To date, the best performing CZTS solar cells have been deposited on Mo-coated soda lime glass (SLG), a carryover from $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ (CIGS) solar cells where Na diffusion from the SLG into the CIGS layer enhances the power conversion efficiency. Impurity diffusion is also expected when CZTS is deposited on Mo-coated SLG, but SLG hosts many other impurities including K, Ca, Mg, and Al and a systematic investigation of whether these impurities diffuse into CZTS and what effect they may have on the film properties has not been conducted. To this end, we have investigated the effects of these impurities on the microstructure of CZTS films. Thin CZTS films were synthesized via *ex situ* sulfidation of Cu-Zn-Sn films co-sputtered on a variety of substrates, including, SLG, quartz, and Pyrex. The metallic precursor films were loaded into a quartz ampoule with 1 mg of S, evacuated to 10^{-6} Torr, sealed and sulfidized at 600 °C for 8 hours. The

sulfidized films were then characterized using X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Concentration depth profiles were examined using time-of-flight secondary ion mass spectrometry (TOF-SIMS). CZTS films synthesized on SLG have significantly larger grains than films grown on other substrates. We have conducted experiments where identical Cu-Zn-Sn precursor films on quartz were sulfidized both in the absence and in the presence of a bare additional piece of SLG in the sulfidation tube. Remarkably, the grain sizes ($>1 \mu\text{m}$) in CZTS films sulfidized with SLG present are dramatically larger than the grain sizes (100's of nm) in CZTS films sulfidized without SLG. This demonstrates conclusively that impurities in SLG volatilize in a S atmosphere and incorporate into nearby CZTS films synthesized on a quartz substrate. Of all the impurities present in SLG, the TOF-SIMS experiments implicated Na, K and Ca as possible elements responsible for enhanced grain growth. To investigate the effects of these impurities individually, we then introduced very small and controllable amounts of Na, K, or Ca into the ampoule during sulfidation of the CZTS. Impurity amounts as low as 10^{-6} moles of Na or 10^{-7} moles of K loaded into the sulfidation tube resulted in a dramatic increase in grain size for films deposited on quartz, while Ca loading had little effect on the final microstructure. The results presented will demonstrate that subtle changes in impurity types and compositions lead to drastic changes in CZTS films.

Graphene and Other 2D Materials Focus Topic

Room: 104 B - Session GR+EM+NS+PS+SS+TF-MoM

Growth of 2D Materials

Moderator: T. Ohta, Sandia National Laboratories, B.

Ozyilmaz, National University of Singapore

8:20am **GR+EM+NS+PS+SS+TF-MoM1 Using Nitrogenated SiC to Produce Wide-gap Semiconducting Graphene**, *P.I. Cohen*, *S. Rothwell*, University of Minnesota, *L.C. Feldman*, *G. Liu*, Rutgers University, *E.H. Conrad*, *F. Wang*, Georgia Institute of Technology

All carbon electronics based on graphene has been an elusive goal. For more than a decade, the inability to produce significant band gaps in this material has prevented the development of semiconducting graphene. While chemical functionalization was thought to be a route to semiconducting graphene, disorder in the chemical adsorbates leads to low mobilities that have proved to be a hurdle in its production. In this work we demonstrate a new approach to produce semiconducting graphene that uses a small concentration of covalently bonded nitrogen, not as a means to functionalize graphene, but instead as a way to constrain and bend graphene. First, about half a monolayer of nitrogen was adsorbed onto a carbon-polar SiC(000-1) surface by annealing in NO. X-ray photoelectron spectroscopy (XPS) indicates that the layer of N that is introduced forms both C=N and C-N bonds that are stable up to 1550C. Then graphene is grown using a controlled silicon sublimation technique, producing, in this case, 3 or 8 layers of graphene. The N coverage and bonding during this process is determined from the XPS signal. After graphene growth the N coverage is about 7 at. % with its bonding unchanged. Examination of the peak intensity in variable energy XPS suggests that the N remains at the interface and there are no other peaks normally associated with either intercalated or substitutional N in graphene. Scanning tunneling microscopy (STM) confirmed that for the case of either 3 layer or 8 layer graphene, N was not present in the top layer. STM, however, showed that the graphene sheet is buckled with 2-4 nm wide folds. The folds can meander and are 5-25 nm long. In addition, atomic resolution images show that the folds are part of a continuous graphene sheet. The implication is that sp³ bonded N at the interface produces this buckling. Finally, angle resolved photoelectron spectroscopy from the buckled, 3-layer graphene is dramatically different than that from pristine 3-layer graphene. With N at the interface, a bandgap of at least 0.7 eV is resolved, presumably due to a finite size effect. For both 3-layer and 8-layer graphene the Fermi velocity is 0.8×10^6 m/s.

9:00am **GR+EM+NS+PS+SS+TF-MoM3 Graphene Growth on C-face SiC in Argon**, *Z. Robinson*, *G.G. Jernigan*, *K. Bussmann*, *R.L. Myers-Ward*, *V.D. Wheeler*, *L.O. Nyakiti*, U.S. Naval Research Laboratory, *S. Oida*, *J. Hannon*, IBM T.J. Watson Research Center, *M. Currie*, *C. Eddy*, *D.K. Gaskill*, U.S. Naval Research Laboratory

Graphene growth on Si-face SiC has been shown to have improved uniformity when synthesized in an argon environment instead of in UHV. For C-face growth, which is expected to yield graphene with superior electronic properties due to the absence of the interfacial layer, similar progress has not yet been achieved. It has been shown that growth by confinement controlled sublimation, where the C-face SiC is put in a graphite pillbox during growth, can result in improved quality graphene

* TFD James Harper Award Finalist

films. However, it remains unclear whether growth by low pressure sublimation (LPS) in a conventional furnace with an argon overpressure can achieve uniformity and thickness control similar to the Si-face. Therefore, a systematic study of SiC surface preparation by hydrogen etching and subsequent graphene growth in argon has been carried out for C-face SiC substrates in a commercially available Aixtron CVD reactor that has been modified for LPS. This reactor exhibits laminar Ar flow and a uniform temperature profile. In this system, which has the advantage of being able to subject different substrates to identical growth conditions simultaneously, it has been found that relatively small differences in the substrate, such as polytype, can have a drastic effect on the resulting graphene film. In fact, growth conditions that result in complete coverage of at least a single layer of graphene on a nominally on-axis 4H substrate have been shown to result in 60% coverage for a nominally on-axis 6H substrate. Therefore, it has been found that optimizing the growth conditions for a particular substrate is crucial if graphene thickness and uniformity are to be controlled. Additionally, it has been suggested that unintentional oxidation of the SiC substrate during growth in high pressures of argon is a potential cause for the non-uniform growth that is observed on the C-face [1]. Several experiments in which LPS grown C-face graphene was transferred to a UHV system equipped with *in situ* XPS have been conducted, and it has been found that UHV anneals of up to 1200 °C were necessary in order to desorb the oxygen. Following the anneal, exposure to atmospheric conditions resulted in the return of only ~20% of the original oxygen concentration. This suggests that a robust oxide which is stable at high temperature may be influencing the graphene growth process. A detailed LEED, LEEM and STM study has been initiated to determine the effect that this oxygen has on the graphene film's properties and new results will be presented.

References:

[1] L. Srivastava, G. He et al., Phys. Rev. B 82, 235406 (2010)

9:20am **GR+EM+NS+PS+SS+TF-MoM4 Microscopic Control of Epitaxial Graphene on SiC(111) and SiC(100) Thin Films on a Microfabricated Si(100) Substrate**, *H. Fukidome, T. Ide, M. Suemitsu, Y. Kawai*, Tohoku University, Japan, *T. Ohkouchi, M. Kotsugi, T. Kinoshita*, JASRI/SPring-8, Japan, *T. Shinohara, N. Nagamura, S. Toyoda, K. Horiba, M. Oshima*, University of Tokyo, Japan

Graphene is the promising material for the next-generation devices due to its excellent electronic properties. We have developed epitaxy of graphene on SiC thin films on Si substrates (GOS) toward fusion of graphene with Si-based electronics. We have found that structural and electronic properties of graphene are tuned by crystallographic orientation of the Si substrates [1,2]. This result indicates that, in combination with Si microfabrication technologies, the electronic properties of GOS may be tuned by microfaceting Si surface [3].

A Si(100) substrate was fabricated by combining electron-beam lithography [3] and alkaline etching which produces (111) and (100) microfacet on the Si(100) substrate. On the microfabricated Si(100) substrate, SiC thin films were grown by using gas-source MBE, followed by graphitization in vacuum at 1500 K. Microscopic characterization of graphene was performed by using 3D NanoESCA for microscopic XPS (micro-XPS) and low-energy electron microscope for microscopic low-energy electron diffraction (micro-LEED). Vibrational and bandstructure characterization was done by Raman microspectroscopy.

The micro-LEED observation reveals that graphene is Bernal stacked on the SiC(111)/Si(111) facet, while it is non-Bernal stacked on the SiC(100)/Si(100) microfacet. The observation is in consistent with the previous result on the epitaxy of graphene on non-fabricated SiC(111)/Si(111) and SiC(100)/Si(100) [1, 2]. The variation of the stacking is explained by the micro-XPS observation. The buffer layer which works as a template for the epitaxy of graphene exists only in between graphene and the SiC(111)/Si(111) microfacet. The existence of the buffer layer is also confirmed by cross-sectional transmission electron microscopy observations. Furthermore, Raman microscopy reveals that the band dispersion (splitting) microscopically changes depending on the variation of the stacking with the microfacet.

Our work can open a new way to microscopically tune control of electronic properties of graphene, semiconductive or metallic, which can make graphene devices multi-functionalized on Si substrates.

One of the authors (H. F.) acknowledges a financial support by KAKENHI (23560003).

References: [1] H. Fukidome et al., J. Mater. Chem. 21 (2011) 17242. [2] H. Fukidome et al., Appl. Phys. Exp. 4 (2011) 115104. [3] H. Fukidome et al., Jpn. J. Appl. Phys. 51 (2012) 06FD02.

9:40am **GR+EM+NS+PS+SS+TF-MoM5 STM Studies on Direction-Selective Epitaxial Graphene: Growth Mechanism and Moiré Superstructures**, *H. Lim, Y. Kim*, RIKEN, Japan

Chemical vapor deposition on a Cu surface is one of the feasible methods for industrial applications, because large-area monolayer graphene film can be achieved.¹ However, grain boundaries and wrinkle formation in the graphene film are known to reduce the electrical performance of graphene. An atomic scale understanding of the growth mechanism on a Cu substrate is therefore of great importance for the synthesis of higher-quality graphene films.

Herein, we present the direction-selective growth of epitaxial graphene (EG) on a Cu(111) surface. All EGs had an identical $R0^\circ$ rotational angle with respect to the lattice direction of Cu(111), although it is distinguished from the general understanding that graphene grown on weakly-interacting metal surfaces generally shows various rotation angles.² The EG growth mechanism was also elucidated with microscopic evidence of characteristic step edge formation of the Cu layers underneath individual EGs. We also observed various kinds of Moiré patterns in EGs with an identical rotational angle. The variety of Moiré patterns, even with an identical rotational angle, cannot be explained by conventional analysis showing that different rotational angles induce the different types of Moiré patterns. We suggest a “compressive strain” effect to explain the various Moiré superstructures observed in the atomically-resolved STM images.

1. Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, 324, (5932), 1312-1314.

2. Batzill, M. *Surf. Sci. Rep.* **2012**, 67, (3-4), 83-115.

10:00am **GR+EM+NS+PS+SS+TF-MoM6 Epitaxial Graphene on Ag(111)**, *B.T. Kiraly*, Northwestern University, *E. Iski*, Argonne National Laboratory, *A.J. Mannix*, Northwestern University, *B. Fisher*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

Graphene plasmonics has recently combined near field optics with the exotic properties of graphene to demonstrate remarkable optical, biochemical, and optoelectronic architectures capable of extreme light concentration and manipulation, highly efficient photoconversion, and single molecule detection. Graphene's unique electronic structure and chemical stability make it an optimal platform to interface with both light and matter; however, current devices are limited by the low-throughput or non-pristine processing steps to produce either the exfoliated or CVD transferred graphene, respectively. In this regard, it would be highly useful to grow a layer of graphene directly on top of a plasmonic metal substrate.

In this work, we report the novel growth of graphene on a bare Ag(111) single crystal. Growth was accomplished by evaporating atomic carbon onto a Ag(111) surface at elevated temperatures under ultra-high vacuum (UHV) conditions. The growth was verified and examined in-situ via scanning tunneling microscopy (STM)/scanning tunneling spectroscopy (STS) and further qualified via ex-situ Raman spectroscopy, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). While the minimal C solubility in Ag suggests similar growth behavior to other noble metals (Cu, Au), this growth mode demonstrates markedly different signatures: nanoscale dendritic features, both terrace and step nucleation, strong electronic scattering at the graphene boundaries, and highly mobile Ag adatoms interacting with the graphene growth front. Furthermore, the growth was carried out at temperatures (600°C-700°C) much lower than the temperatures commonly used for conventional chemical vapor deposition (CVD) techniques (>1000°C) and it could be extended to a variety of weakly interacting substrates, including non-metals. All the observed growth was electronically characterized as single-layer graphene, and was further supported by the narrow full-width half-maximum (FWHM) of the 2D Raman band. All the observed growth was electronically characterized as single-layer graphene, and was further supported by the narrow full-width half-maximum (FWHM) of the 2D Raman band. A 65% decrease in the Ag-O peak in the O1s spectrum reveals that the graphene layer protects the underlying silver from environmental degradation. Two predominant Moiré patterns were observed in the graphene; their periodicity was ~1.55nm and ~0.95 nm corresponding to lattice offsets of ~4.5° and ~13°, respectively. Finally, the graphene grown on Ag is weakly bound to the surface indicated by the stark contrast between the dI/dV spectra of the graphene and bare silver surface. The graphene-Ag system demonstrated in this study could immediately be applied to tip-based molecular spectroscopies and will lead to the development of more advanced hybrid graphene plasmonics.

10:40am **GR+EM+NS+PS+SS+TF-MoM8 A Universal Scheme to Convert Aromatic Monolayers Into Functional Carbon Nanomembranes**, A. Angelova, H. Vieker, N.J. Weber, D. Matei, University of Bielefeld, Germany, S. Kurasch, U. Kaiser, University of Ulm, Germany, K. Müllen, Max Planck Institute for Polymer Research, Germany, A. Götzhäuser, A. Turchanin, University of Bielefeld, Germany
The engineering of free-standing nanomembranes with molecular or atomic thickness and with well-defined structural and functional properties is a challenge for materials research. Here we present a broadly applicable scheme to create mechanically stable carbon nanomembranes (CNMs) with a thickness of ~0.5 to ~3 nm. Monolayers of polyaromatic molecules (oligophenyls, hexaphenylbenzene and polycyclic aromatic hydrocarbons) were assembled and exposed to electrons that crosslink them into CNMs; subsequent pyrolysis converts the CNMs into graphene sheets. In this transformation thickness, porosity and surface functionality of the nanomembranes are determined by the monolayers, and structural and functional features are passed on from the molecules through their monolayers to the CNMs and finally on to the graphene. Our procedure is scalable to large areas and allows the engineering of ultrathin nanomembranes by controlling the composition and structure of precursor molecules and their monolayers.

11:00am **GR+EM+NS+PS+SS+TF-MoM9 Hydrogenation of Monolayer and Bilayer Graphene and Nanodiamond Growth on Ni(111) Substrate**, I.I. Oleynik, L. Adamska, M. Batzill, University of South Florida

Hydrogenation of a few layer graphene is known to result in the change of sp^2 to sp^3 hybridization, which can be exploited to grow nanodiamond thin films. First-principles studies of hydrogenated monolayer, bilayer, and tri-layer graphene, supported on Ni(111) substrate are performed using first-principles density functional theory. The monolayer graphene and AB-stacked bilayer graphene are shown to rehybridize to form sp^3 bonds, thus promoting the formation of nanodiamond thin films. Structural, electronic and magnetic properties of the hydrogenated monolayer, bilayer, and tri-layer graphene are discussed.

11:20am **GR+EM+NS+PS+SS+TF-MoM10 Graphene-based, Graphene-derived, and New Carbon Materials**, R.S. Ruoff, The University of Texas at Austin

INVITED
Graphene-based materials are of interest because of their electronic and thermal transport, mechanical properties, high specific surface area, and that they can act as an atom thick layer, barrier, or membrane, among other reasons. Our micromechanical exfoliation approaches [1,2] conceived of in 1998 yielded multilayer graphene and one paper described in detail how monolayer graphene could be obtained [1]. Three main research areas of our group are: (i) Growth of large area graphene on metal substrates, characterization and physical properties, and studies of devices having such CVD-grown graphene as a central component; (ii) Generation, study, and use of chemically modified graphene 'platelets' (typically derived from graphite oxide) including as dispersed in liquids forming colloids, and powders derived from such colloids or separately generated by microwave or thermal treatment of graphite oxide; (iii) Generation and study of new types of carbon derived from graphene-based precursors, such as *activated microwave expanded graphite oxide* ('aMEGO')[3].

Here, I will focus on growth of graphene and h-BN from research projects underway in my group and also *briefly* describe what I think are some important new directions in carbon and *first row element* research, for the next 10-20 years, that will introduce new issues involving interfaces for these new material classes that have not yet been made experimentally [4].

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2. Lu XK, Huang H, Nemchuk N, and Ruoff RS, *Patterning of highly oriented pyrolytic graphite by oxygen plasma etching*, Applied Physics Letters, **75**, 193-195 (1999).
3. Zhu, Yanwu; Murali, Shanthi; Stoller, Meryl D.; Ganesh, K. J.; Cai, Weiwei; Ferreira, Paulo J.; Pirkle, Adam; Wallace, Robert M.; Cychosz, Katie A.; Thommes, Matthias; Su, Dong; Stach, Eric A.; Ruoff, Rodney S. *Carbon-Based Supercapacitors Produced by Activation of Graphene*. Science **332**, 1537-1541 (2011).
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Plasma Science and Technology
Room: 102 B - Session PS+AS+BI+SE-MoM

Atmospheric Plasma Processing: Fundamental and Applications

Moderator: M.A. Lieberman, University of California, Berkeley

8:20am **PS+AS+BI+SE-MoM1 Field Emission in Microscale Dimensions: A New Approach to Atmospheric Pressure Gas Discharges**, Y. Li, P. Rumbach, D.B. Go, University of Notre Dame

INVITED
Electron field emission is traditionally considered a low-pressure phenomenon and most field emission-based technologies, such as scanning electron microscopes, generate field emission under high vacuum conditions. However, over the course of past decade, advances in microscale devices have led to the field emission devices that operate at high pressures, including at and near to atmospheric pressure. At these pressures, the field-emitted electrons can ionize the interstitial gas between the electrodes, leading to the formation of gas discharges. With emerging applications in gas sensing and gas reforming, this new approach to gas discharges not only introduces new, interesting physics but also offers many new technological opportunities. This work will focus on the theory and generation of stable, field emission-driven Townsend discharges. The physical concepts underpinning these discharges will be discussed as theoretical and modeling efforts have highlighted many significant features of this discharge mode – including very high electron densities ($\sim 10^{14} \text{ cm}^{-3}$) and highly non-Maxwellian electron densities. Experimental studies and the role of the cathode material will also be discussed as evidence of pressure scaling for field emission will be presented. Finally, new applications and future opportunities for discovery will be covered.

9:00am **PS+AS+BI+SE-MoM3 Simulation of Microplasma Based Pressure Sensors**, J.-C. Wang, Z. Xiong, C. Eun, X. Luo, Y. Gianchandani, M.J. Kushner, University of Michigan

Pressure monitors in hostile environments often use piezoresistive and capacitive based sensors. The smallest dimension of this class of sensors is about 1 mm. Recently, a microplasma-based pressure sensor has been developed which is capable of dimensions at least an order of magnitude smaller. In these sensors, a plasma is initiated between an anode and two competing cathodes in a sealed chamber having a diaphragm as one surface. External pressure deflects the diaphragm which changes the inter-electrode spacing for one of the anode-cathode pairs, thereby redistributing the current collected by the two competing cathodes. Pressure is then proportional to the relative difference in current collected by the two cathodes.

In this presentation, we will discuss the properties of microplasma-based pressure sensors using results from a two-dimensional simulation. The model, *nonPDPSIM*, solves Poisson's equation, transport equations for charged and neutral species, and the electron energy conservation equation for electron temperature. Radiation transport is addressed using a Green's function approach, and sheath accelerated electrons are addressed using Monte Carlo methods. The microplasma is sustained between an anode (A) biased with hundreds of volts and two grounded cathodes (K_1 , K_2) in a sealed chamber filled with 1 atm of Ar or rare gas mixtures. The reference cathode (K_1) is located adjacent to the anode while the sensing cathode (K_2) is mounted on the diaphragm separated by a gap of 10 to 100 μm . We find that following a small amount of electric field emission of electrons from the edges of K_1 and K_2 , the electrons rapidly avalanche in the geometrically enhanced electric field at the edge of the anode and creates a conductive plasma within tens of ns. The current distribution on K_1 and K_2 varies with inter-electrode spacing (AK_2) which is changed by deflection of the diaphragm due to the external pressure. The current distribution can also be optimized by adjusting the impedance connected to electrodes.

*Work was supported by the Advanced Energy Consortium.

9:20am **PS+AS+BI+SE-MoM4 A Flexible Paper-based Microdischarge Array Device for Maskless Patterning on Nonflat Surfaces**, Y.J. Yang*, M.Y. Tsai, W.C. Liang, H.Y. Chen, C.C. Hsu, National Taiwan University, Taiwan, Republic of China

This study presents a simple and economical paper-based microdischarge array for maskless surface patterning under atmospheric pressure condition. This paper-based system is a dielectric-barrier-discharge (DBD)-type device and stable plasmas can be sustained in an array of cavities. Due to its

*** Coburn & Winters Student Award Finalist**

flexible feature, this paper-based device allows for performing non-flat surface patterning processes with a feature size down to 500 μm . When a flat or a curved glass surface with 6 mm in its curvature is directly treated by the Ar plasma generated by this device, hydrophilic spots can be generated on the flat or curved surface, respectively. While using tetraglyme as the precursor in Ar atmosphere, this paper-based device is able to perform plasma polymerization and to pattern polyethylene oxide (PEO)-like array of patterns on glass surfaces. Under this arrangement, the optical emission spectrum emanating from the plasma show CO emissions at 561 nm during the deposition process, suggesting that the participation of precursor molecules in the process. The FTIR spectra of deposited films show absorption of C-O-C bonding at 1100 cm^{-1} , indicating retaining of ether groups. To test the anti-fouling property of this film, Alexa Fluor 546-conjugated fibrinogen was utilized as a model reporter molecule for protein absorption test. The fluorescence image shows clear contrast between the coated and non-coated area. The PEO-pattered regions appear to be dark since no protein absorption occurs. This work demonstrates a flexible and cost-effective approach to pattern flat and non-flat surfaces with a maskless process. This work was supported by National Science Council of Taiwan, the Republic of China (101-2221-E-002-163-MY2)

9:40am **PS+AS+BI+SE-MoM5 Hydrophobic Fluorocarbon Films Synthesized from Liquid Monomers by Atmospheric Pressure Plasma**, *J. Hubert, N. Vandecasteele, T. Dufour*, Univ. Libre de Bruxelles, Belgium, *C. Poleunis*, Univ. catholique de Louvain, Belgium, *P. Laha*, Vrije Univ. Brussel, Belgium, *P. Viville*, Materia Nova, Belgium, *A. Delcorte, P. Bertrand*, Univ. catholique de Louvain, Belgium, *H.A. Terry*, Vrije Univ. Brussel, Belgium, *R. Lazzaroni*, Materia Nova, Belgium, *F.A.B. Reniers*, Univ. Libre de Bruxelles, Belgium

The exceptionally low surface energy of polytetrafluoroethylene (PTFE), due to the CF_2 functional groups present on its surface gives the polymer advantageous properties such as hydrophobicity. In order to create PTFE-like films, low pressure plasma deposition of fluorocarbon films has been extensively studied in the last decade. These works focus however on the use of gaseous precursors such as CF_4 , C_2F_6 or C_4F_8 .

In the present study, hydrophobic fluorocarbon coatings have been synthesized from two different precursors, which are liquid at room temperature. Perfluorohexane (C_6F_{14}), a fully saturated monomer and perfluoro(2-methylpent-2-ene) (C_6F_{12}) containing one unsaturated bond are injected in a dielectric barrier discharge (DBD) by a continuous argon or helium flow. In order to characterize the plasma polymer films and the texturization process, both, analysis of the surface and the gas phase have been performed.

Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) measurements have been performed to highlight the structure and composition of the C_xF_y films depending on the Yasuda factor (W/FM), throughout the influence of the power and the monomer flow rate. Water contact angle (WCA) measurements have shown that the hydrophobicity properties of the fluorocarbon films were similar to that of PTFE as WCA of 110° have been obtained. However, the structure also depends on the nature of the carrier gas (argon or helium) and in some cases, WCA as high as 140° were achieved. Atomic force microscopy AFM measurements are used to correlate the increase in hydrophobicity with the increase in roughness, which could be linked to the film thickness.

In order to complete the analysis of the polymerization process, mass spectrometry (MS) and optical emission spectroscopy (OES) have been performed. Fluorocarbon compounds such as CF , CF_2 , CF_3 , or higher mass fragments such as C_3F_3 or C_2F_4 have clearly been identified. Their detection combined to the SIMS analysis could help us to understand the polymerization mechanism/reaction of the two precursors.

10:00am **PS+AS+BI+SE-MoM6 Deciphering Gas-Phase and Solution-Phase Reactions Initiated by Plasmas at the Surface of Aqueous Solutions**, *P. Rumbach*, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University, *D.B. Go*, University of Notre Dame

Recent advancements in atmospheric-pressure plasma technology have enabled applications in polymer processing, plasma medicine, and water treatment. Many of these applications rely heavily on physical and chemical interactions between plasmas and aqueous solutions. We have recently shown that plasma electrons are involved in electrolytic reactions such as the reduction of aqueous hydrogen ions (H^+) to hydrogen gas[1]. In this work, we show that the reactions are more complex and involve a competition between plasma chemistry and solution chemistry.

To study interactions between a plasma and liquid, saline solutions were exposed to an argon (Ar) DC microplasma jet, and the effects of various reactions occurring in the plasma and solution phase were characterized. When the plasma jet was run in a background of argon or oxygen gas, traditional electrolytic reactions yielding sodium hydroxide (NaOH) were found to be dominant, making the solution more basic ($\text{pH} \sim 8$). Running

the plasma jet in a background of atmospheric air produced significant amounts of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) in solution. Production of HNO_3 in air typically occurs at a rate two orders of magnitude higher than NaOH, making the solution more acidic ($\text{pH} \sim 3$). In a background of nitrogen gas, HNO_3 was also produced, but at a rate that is limited by oxygen gas evolution from water electrolysis. Overall, the chemical composition of the solution is affected by both electrolytic reactions at the plasma-liquid interface as well as reactions occurring in the bulk plasma.

[1] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **45**, 442001 (2012).

10:40am **PS+AS+BI+SE-MoM8 Prostate Cancer Treatment using Low-Temperature Atmospheric Pressure Plasmas: Advanced Optical Diagnostics and Multi-scale Numerical Simulations**, *D. O'Connell*, University of York, UK

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. Plasmas have the advantage of delivering these components simultaneously providing potentially superior processes through synergies. This has led to the establishment of low-temperature plasmas with potential in disease therapeutics and plasma pharmacology. The challenges lie in understanding the mechanism of interaction, quantifying and accurately tailoring the plasma and its power dissipation. Suitable optimized plasma sources are currently lacking, and improbable through empirical investigations. Therefore, quantifying the power dissipation and energy transport mechanisms through the different interfaces from the plasma regime to ambient air, towards the liquid interface and associated impact on the biological system through a new regime of liquid chemistry initiated by the synergy of delivering multiple energy carrying species, is crucial.

This presentation will include examining our interaction studies of atmospheric pressure plasma jets with prostate cancer cells and our results of employing advanced diagnostic techniques for direct measurements of reactive plasma species and comparison to chemical kinetics simulations. These include absolute densities of atomic oxygen and atomic nitrogen using non-linear laser spectroscopy and vacuum ultra-violet (VUV) absorption spectroscopy, where the VUV radiation was produced using a synchrotron and detected with a high-resolution Fourier-transform spectrometer.

11:20am **PS+AS+BI+SE-MoM10 Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Scaffolds Using Plasma Enhanced Chemical Vapor Deposition**, *M. Hawker, A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Bioresorbable polymers such as poly(ϵ -caprolactone) (PCL) have a multitude of potential biomaterial applications such as controlled-release drug delivery and regenerative tissue engineering. Fabricating these polymers into porous, three-dimensional (3D) materials is critical for such biological applications to maximize their surface-to-volume ratio, mimic the extracellular matrix, and increase drug-loading capacity. Three-dimensional porous PCL scaffold materials have been fabricated via the porogen leaching method. These scaffolds can be plasma-treated to improve or modify their surface properties while maintaining the desirable bulk polymer characteristics. For example, plasma polymerization can be used to encapsulate the polymer scaffold, thereby potentially providing a mechanism for controlled release drug delivery. Here, two different fluorocarbon (FC) precursors, octofluoropropane (C_3F_8) and hexafluoropropylene oxide (HFPO), were used to deposit FC films on PCL scaffolds using plasma enhanced chemical vapor deposition. X-ray photoelectron spectroscopy (XPS) analysis showed that high- CF_2 content films were deposited on the PCL scaffolds, similar to those previously deposited in our labs on one-dimensional and two-dimensional materials. Cross-sectional XPS data demonstrated that FC film deposition occurred both on the outer scaffold surface and throughout the 3D structure. Scanning electron microscopy data confirmed that FC film deposition yielded conformal rather than blanket coatings as the porous scaffold structure was maintained after plasma treatment. Additional parameter studies suggest that treatment time, substrate location, and precursor gas have significant impact on the nature of the deposited films. This work demonstrates that conformal FC coatings can be deposited on 3D polymeric scaffolds using plasma processing. Results from cell adhesion studies as well as other film deposition systems and alternate bioresorbable scaffold materials will also be presented.

11:40am **PS+AS+BI+SE-MoM11 Deactivation of Lipopolysaccharide by an Atmospheric Pressure Plasma Jet**, *E.J. Bartis, C. Hart, Q. Yang*, University of Maryland, College Park, *T.-Y. Chung, D.B. Graves*, University of California, Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland, College Park

Low temperature plasma treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules. However, a major knowledge gap exists regarding which plasma species are responsible for the modifications required for deactivation. Lipopolysaccharide (LPS) and lipid A, the toxic element of LPS, are the main components of the outer membrane of Gram-negative bacteria and induce a strong immune response in animals. In this study, LPS-coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. Additionally, spatially-resolved optical emission spectroscopy, UV absorption spectroscopy, and electrical characterization were performed on the jet to identify and characterize plasma-generated species. Biological activity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA) and correlated with changes in surface chemistry measured by vacuum transfer to x-ray photoelectron spectroscopy (XPS). The kHz-driven atmospheric pressure plasma jet consists of two tubular electrodes surrounding an alumina tube. By flowing Ar with small admixtures of O₂/N₂ through the tube and applying a high voltage across the electrodes, the plasma ignites to form a stable jet. The species that arrive at the sample can be regulated by adjusting the distance from the source to the sample. At longer source-to-sample distances, species with short lifetimes will not reach the sample. Adding oxygen to the gas flow causes the most significant changes. For source-to-sample distances > 10 cm, where radical species dominate, higher levels of deactivation were observed for O₂/Ar plasma than for Ar and N₂/Ar plasmas. O₂/N₂/Ar plasma showed decreased deactivation compared to O₂/Ar plasma with the same O₂ admixture due to creation of NO_x, whose formation consumes reactive oxygen species. With XPS, we observed that O₂-containing discharges remove C-C bonding from the surface while N₂-containing discharges cause minimal changes. XPS studies of APPJ-treated films showed that deactivation depends on C-C bonding measured in the C 1s, which depends on the admixture of O₂ into the APPJ. The decrease in C-C bonding correlates with the loss of lipid A's aliphatic chains, which are partially responsible for its toxicity. The authors gratefully acknowledge financial support from US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

Plasma Science and Technology Room: 104 C - Session PS-MoM

Innovative Chemistries for Advanced Etch Processes Moderator: J.P. Chang, University of California at Los Angeles

8:20am **PS-MoM1 Effects of Plasma-Induced Si Damage Structures on Annealing Process Design—Gas Chemistry Impact**, *A. Matsuda, Y. Nakakubo*, Kyoto University, Japan, *M. Fukasawa*, Sony Corporation, Japan, *Y. Takao, K. Eriguchi*, Kyoto University, Japan, *T. Tatsumi*, Sony Corporation, Japan, *K. Ono*, Kyoto University, Japan

Plasma-induced Si substrate damage during shallow trench isolation, 3D-fin, and gate electrode formation processes have been believed to lead to "Si recess" (Si loss) [1] and latent defect generation resulting in performance degradation of metal-oxide-semiconductor field-effect transistor (MOSFET)—an off-state leakage (power consumption) increase [2] and the drain current (chip clock-frequency) decrease [3], respectively. Various plasma gas chemistries are employed for these Si etching processes. Regarding annealing process parameters, it was reported [4] that conventional thermal budgets could no longer be applied—the annealing temperature might be primal—in particular, in the case of hydrogen-containing plasmas (HBr/O₂- and H₂-processes). Based on this finding, two questions may be pointed out; (1) does this temperature-dependent feature hold for other plasmas? and (2) what is the principal mechanism? To answer these questions, Si-damage formation and the following annealing mechanisms were comprehensively investigated for various plasma processes (HBr/O₂, H₂, Ar, and He) and annealing conditions (750–1050°C) in this study. An electrical capacitance–voltage (C–V) technique was employed to quantitatively evaluate the plasma-induced defect density, and a molecular dynamics simulation was carried out to study in detail the localized defect structures.

Silicon wafers covered with thermal oxide layer (2 nm) were damaged by various plasma processes and annealed in N₂ ambient with various

conditions. Defect densities before and after annealing were quantified by 1/C²-based analysis. It was found that the temperature-dependent damage-recovery dynamics holds for overall plasma processes, although H₂- and He-plasma damage exhibit complicated features. We speculate that both the localized defect structure with its low density (10¹⁸–10¹⁹ cm⁻³) and the profile in the damaged region play major role in this mechanism—being confirmed also from molecular dynamics simulations. The present findings imply that not only the defect structure but also the profile in the damaged region should be identified in advance for designing the annealing conditions in future advanced MOSFET process technologies.

[1] M. Fukasawa *et al.*: *J. Vac. Sci. Technol.* **A 29**, 041301 (2011).

[2] K. Eriguchi *et al.*: *J. Vac. Sci. Technol.* **A 29**, 041303 (2011).

[3] K. Eriguchi *et al.*: *IEEE Electron Device Lett.* **EDL-30**, 1275 (2009).

[4] Y. Nakakubo *et al.*: AVS 59th Annual International Symposium and Exhibition, PS-MoM10 (2012).

8:40am **PS-MoM2 Advancing Patterning Processes Further by Employing a New Gas**, *S.U. Engelmann, E.A. Joseph, R.L. Bruce, H. Miyazoe, W.S. Graham, E.M. Sikorski*, IBM T.J. Watson Research Center, *M. Nakamura, T. Suzuki*, Zeon Chemicals LP, *H. Matsumoto, A. Itou, T. Suzuki*, Zeon Corporation

Improving patterning processes is a very crucial element of advancing microelectronics manufacturing processes. Deformation of organic soft masks is a very commonly observed phenomenon. Other issues include extensive plasma damage or mask retention for post-lithography solutions. [1]

Our team has recently introduced a new etch gas which is able to etch by selective deposition of a fluorocarbon layer, [2] analogue to the well established oxide etch mechanism commonly used in manufacturing. [3] Selective deposition was achieved by redesigning the FC etch gas, where reaction with a nitride substrate layer reduces the FC film thickness compared to silicon or oxide substrates. This mechanism was most prominently applied to the spacer module, where high selectivities to oxide and silicon substrates is required. In contrast to conventional spacer processes, an excellent resistance to PR materials opened the processing capabilities for this new gas tremendously.

We will demonstrate how this new gas can be used in patterning solutions, where a high degree of accuracy is needed. The wiggling performance of the new gas will be discussed, as well as direct patterning and/or trilateral patterning using the new gas. Lastly, we also evaluated the new gas for applications beyond optical lithography.

[1] S. Engelmann *et al.*, *Proc. SPIE* 8328-9

[2] S. Engelmann *et al.*, AVS 58th Int. Symp. & Exhibit. (2011)

[3] M. Schaepekens *et al.*, *J. Vac. Sci. Technol.* **A 17**, 26 (1999)

9:00am **PS-MoM3 Advanced Etching Gas Development for High Aspect Ratio Structures**, *R. Gupta, C. Anderson, V. Surla, B. Lefevre, V. Pallem, N. Stafford*, Air Liquide

In order to enable high aspect ratio etching capabilities in materials such as SiO and SiN, it is highly desirable to determine what role the plasma etch chemistry can play. Both saturated and unsaturated fluorocarbons have been introduced over the years, as well as simple hydrofluorocarbon molecules. Mixtures of the above are often employed to allow control of etching species in the plasma recipe. In this work we systematically study the role of the gas molecule structure on the etching behavior that can be achieved. The ultimate goal is to identify ideal candidate molecules that will allow achieving the future process requirements.

This study will provide a comparative study of fluorocarbon-based etch chemistries, wherein a 200mm dual-CCP tool has been employed to produce high aspect ratio structures. By studying the specific effects of H, C=C double bonds, F:C ratio, and molecule structure, we can identify relationships to the etching performance. The model chemistries for this work include both cyclic- and linear-type structures. The performance of each molecule is initially studied on blanket wafers, measuring etch rates of silicon oxide, silicon nitride, amorphous carbon, and undoped poly-Si. For selected conditions of optimized etch rate and mask selectivity, 100nm trench width patterns are also etched and examined in cross-section SEM.

In order to develop a strong correlation between etch performance and the molecule structure, we perform mass spec measurements of the gases by direct injection of the fluorocarbon gas, measuring the electron-impact fragmentation of each gas. Electron energies from 10-100 eV are recorded, and the relative abundance of each fragment species is plotted against the electron energy. By studying the dominant fragments, we observe that oxide etch rate and mask selectivity can be predicted based on the C:F ratio of majority species.

9:20am **PS-MoM4 Highly Selective Etch of PMMA to PS for DSA Lithography by Using Carbon Containing Gas 100 MHz CCP RIE System.** *T. Imamura, H. Yamamoto, M. Omura, I. Sakai, H. Hayashi,* Toshiba Corporation Semiconductor Company, Japan

As critical dimension (CD) continue to shrink, optical lithography has become increasingly difficult. Directed-self assembly (DSA) of block copolymer (BCP) is a promising candidate for a low cost 1X patterning process. CD of DSA lithography is determined by composition of the BCP. 12.5 nm hp patterns is formed using polystyrene-block-poly methyl methacrylate (PS-b-PMMA) [1]. DSA lithography process using PS-b-PMMA needs selective removal of PMMA to PS, which is called "development process". Wet development process has enough selectivity, but there is a possibility of collapse of the remaining PS pattern. Because this problem arises due to surface tension of liquid, it is difficult to solve in principle. Dry development process has an advantage in that point. Generally, O₂-based plasma is used for the PMMA removal and selectivity is around 2. Some have reported that the selectivity exceeds 4 by keeping the ion bombardment energy low in O₂/Ar plasma. Also, because we use the remaining PS pattern as a mask of underlayer etch, high selectivity is needed to keep the PS pattern thick.

In this study, we focused on differences of material components of PS and PMMA. Based on that the PMMA has more oxygen in the film than in PS, we designed a new gas chemistry using carbon containing gas to realize high selective PMMA to PS etching.

Single layer film of PS and PMMA were spin-coated on a silicon wafer, and then baked. The thicknesses were 240 nm and 340 nm, respectively. We used 100 / 13.56 MHz dual frequency superimposed (DFS) capacitive coupled plasma (CCP) system. Plasma etching conditions were as follows. The pressure was 10 mTorr, 100MHz RF power 700W, 13.56 MHz RF power 70W, substrate temperature 40°C, and the total flow rate of the gas mixture of carbon containing gas and Ar was 300sccm. We changed the flow rate ratio of carbon containing gas and measured the film thickness by ellipsometry measurement.

When the carbon-containing gas ratio was increased from 7% to 10 % and 13 %, both the PMMA and PS etch rates decreased. The etch rate of PMMA decreased slightly, from 42.4 to 39.6 and 38.2 nm/min, while the rate of PS decreased drastically, from 5.4 nm/min to 1.8 and 0.3 nm/min. As a result, very high selectivity could be obtained at 13 %. We assumed that carbon atom from carbon containing gas was absorbed on PS and PMMA films. The carbon atoms on PMMA film reacted with oxygen in the film and volatilized as CO or CO₂. On the other hand, the carbon remained on PS film and protected etching. As a result, carbon containing gas plasma achieved highly selective PMMA etching.

Reference

[1] C. Bencher et al., Proc. SPIE 7970, 79700F (2011)

9:40am **PS-MoM5 New Fluorocarbon Free Chemistry Proposed As Solution to Limit Porous SiOCH Film Modification during Etching.** *N. Posseme,* CEA-LETI, France, *L. Vallier,* CNRS-LTM, France, *C.-L. Kao,* AMAT, *C. Lictra,* CEA-LETI, France, *C. Mannequin,* CNRS-LTM, France, *J. Pender, S. Nemani,* AMAT

Today etching processes involved during the porous SiOCH (p-SiOCH) integration combined with a metallic hard mask (MHM) generate serious issues such as film damage, residue growth, bottom line roughness. The last critical issue we are facing today is that the wet cleaning (HF based chemistry) is not efficient enough to remove all the fluorocarbon layer formed on sidewall during etching. Fluorine is remaining on sidewall after wet cleaning. This Fluorine is encapsulated during the metal barrier deposition (prior to copper deposition) and can lead to reliability degradation of the p-SiOCH film. Today there is no solution to this problem except the use of aggressive wet cleaning, inducing in this case important CD loss. In this context we developed a new fluorocarbon (FC) free chemistry solving these issues.

In this work, p-SiOCH (deposited by PECVD, composition: Si 28%, O 29%, C 43%, k= 2.5, porosity <30 %) film modification has been studied using patterned and floating coupons (deposit/film modification formed on the floating sample gives a rough estimation of passivation layer formed on the sidewalls) and characterized by ellipsometry porosimetry (EP), infrared spectroscopy in attenuated total reflection configuration (ATR), X-ray photoelectron spectroscopy (XPS) and dielectric constant measurement comparing the new FC free chemistry to conventional FC (CF₄/C₄F₈/N₂/Ar) chemistry.

It will be demonstrated that the FC free etch chemistry presents a wide process window to adjust the taper profile by playing on plasma parameters with a hardly impact on p-SiOCH film modification (+4% k value increase compared to +16% with conventional FC chemistry, correlated with ATR analyses). The efficiency of wet cleaning to fully remove the passivation

layer formed on sidewalls without degrading the profile will also be presented.

10:00am **PS-MoM6 Characterization of the Effects of Mildly Oxidizing Chemistries on Silicon Oxidation for Advanced Photoresist-Strip Applications.** *B. Thekjoisworo, B. Jacobs, I. Berry, D. Cheung, J. Park,* Lam Research

For the advanced technology nodes, there is a need to strip photoresist quickly while meeting the stringent requirement of ultra-low oxidation and loss of the semiconductor substrate, silicon (Si). Two chemistries, NH₃/O₂ and H₂/N₂, have garnered attention for their ability to strip photoresist reasonably quickly while incurring low material loss. In this work, Si surfaces were exposed to either downstream NH₃/O₂ or H₂/N₂ plasmas, and the effects of these chemistries on Si oxidation were characterized and compared. For the NH₃/O₂ chemistry, Si oxidation was found to occur during the plasma-exposure step, while the extent of post-plasma oxidation was determined to be relatively minor. Accordingly, we evaluated the behaviors of Si oxidation as a function of plasma process parameters, and substrate temperature and NH₃ concentration in the gas feed were determined to exert strong effects on Si oxidation. Specifically, oxidation decreases with increasing temperature and with increasing NH₃ concentration. These process trends provide insight into the mechanism of the Si oxidation as well as to the nature of the radicals that induce the oxidation. Furthermore, the above finding demonstrated that Si oxidation can be controlled through judicious choice of the process parameters. When compared to the NH₃/O₂ (90% NH₃) chemistry, the H₂/N₂ chemistry generally led to lower Si oxide growth. Although the H₂/N₂ chemistry gives rise to lower Si oxidation, the NH₃/O₂ could offer other advantages, such as higher ash rate and better photoresist-residue performance. Therefore, the desired trade-offs among ash rate, residue performance, and level of substrate oxidation will ultimately govern the choice between the two chemistries.

10:40am **PS-MoM8 Challenges in Etching of Multicomponent Oxides and Other Difficult-To-Etch Materials.** *J. Margot,* Université de Montréal, Canada, *M. Chaker,* INRS, Canada **INVITED**

Despite its successful implementation in industry, etching was mainly evolved empirically. Very often recipes are developed by users for specific materials. However the absence of actual scientific investigation considerably limits technology transfer. Therefore, except for a few classical materials like Si et SiO₂, only a limited amount of publications is available for unconventional materials used for example in microelectronics, photonics and telecommunications. Among these more or less exotic materials let us mention ferroelectric materials (PLZT, BST, SBT), electro-optic materials (SrTiO₃, LiNbO₃, CaBaNb₂O₆), metal-insulator transition materials (VO₂), and unconventional conductors (Pt, IrO₂, ITO, LaNiO₃). Optimizing etching processes for such materials is difficult as most of them present a low reactivity with usual etching gases such as fluorinated and chlorinated gases. Their etching is mainly governed by ion sputtering and the reactive gases forming the plasma sometimes interact with materials surface to form compounds that inhibit etching.

In this presentation, we will review the work performed by our group over the last decade on the etching of multicomponent oxides, with a particular focus on the etching of SrTiO₃ and CaBaNb₂O₆. We will also show how simulation can provide information on the redeposition of sputtered species on patterned surfaces, taking as an example the case of an unconventional conductor.

11:20am **PS-MoM10 Thermodynamic Approach to Select Viable Etch Chemistry for Magnetic Metals.** *T. Kim, K. Chen, J.P. Chang,* University of California at Los Angeles

Magnetic tunnel junctions (MTJ) which are based on magnetic hysteresis for data storage are an important part of spin-electronics. An MTJ-based magnetoresistive random-access memory (MRAM) has several advantages, such as nonvolatility, fast writing speeds (2-4 ns). Thus MRAM has the potential to be a universal memory solution. In past few years, some important progress has been reported to fabricate durable, high-yield MTJ arrays, using the advances in materials.

Among the challenges of fabrication, MTJ etching processes is one of the most critical. Ion beam etching was a general etching technique at the beginning of MTJ fabrication, however the etched material tends to re-deposit on the sidewalls and form fences. The approach using a reactive ion etch (RIE) has been recognized as an important strategy for integrating MRAM because it can potentially generate volatile etch products to avoid sidewall re-deposition. Halogen-gas-based RIE processes have been used to etch ferromagnetic layers. Some chemical enhancement induced by RIE has been reported for NiFe and NiFeCo using Cl₂ gases,^[1] however the low etch rate requires high-density plasma conditions.

In this work, a thermodynamic approach is used to assess the feasibility of various etch chemistries, beginning with the consideration of reactions between the dominant vapor phase/condensed species and the surface at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of RIE process.^[2] In this report, a few magnetic metals are considered (Co, Fe, and Ni) along with various halogen and organometallic based chemistries. The thermodynamically favorable reaction has been investigated and the vapor pressure of its product has been calculated. In addition, the vapor pressure enhancement induced by adding secondary gas such as hydrogen has also been studied. Experimental validation is an important part to prove the prediction.

[1] K.B. Jung et al., J. Electron. Mat., 27, 972 (1998)

[2] N.S. Kulkarni et al., J. Electro. Soc., 149, G620 (2002)

11:40am **PS-MoM11 Studies on Highly Selective Si₃N₄ Spacer Etching over Si/SiO₂ using CH₃F/O₂ Plasmas**, *B. Parkinson, A. Raley, A. Ranjan, K. Kumar, P. Biolsi*, TEL Technology Center, America, LLC

Recent advancements in device scaling have led to the widespread introduction of 3-D gate structures (i.e. FINFET, tri-gate). Introduction of 3D structures has increased the challenges of spacer etching. Planner gate structures typically require shorter over-etches (10-30%) and thus requirement of selectivity of spacer film over underlying films (Si and SiO₂) is not as stringent as for 3-D structures. In the case of 3D gate structures, the spacer film will also surround the Si-fins. Surface of Si-fins must be pristine (residue-free and without surface modification) in order for epitaxial silicon growth. Complete removal of SiN around Si-fins typically requires over-etches ranging from 150 to 300%. This dramatic increase in OE time requires an increase in spacer film selectivity to Silicon (fins) and Silicon Oxide (gate-mask and isolation Oxide). CH₃F/O₂ based etching chemistries are typically used to achieve high Nitride-to-Oxide and Nitride-to-Silicon selectivity. This paper explores a CH₃F/O₂ chemistry created in a RLSA™ plasma reactor. The impact of block photoresist masking on oxidation etching mechanisms is presented. An analysis of plasma characteristics using Optical Emission Spectroscopy (OES) is also provided. Experimental results indicate a correlation between ion energy (derived from peak-to-peak voltage, V_{pp}), passivation over SiN/Si/SiO₂ (derived from gas-phase radical concentration) and selectivity. Microwave power and pressure provides control of relative concentrations of etchants/passivants (via control of electron energy distribution) and ion energies can be tuned by bias power. High Nitride-to-Oxide selectivity and minimal Si- and SiO₂-loss can be effectively achieved by balancing passivation layer on SiN/Si/SiO₂ and tuning Microwave Power and pressure to provide optimal V_{pp}.

Monday Afternoon, October 28, 2013

Manufacturing Science and Technology

Room: 202 B - Session MS+AS+EM+NS+PS+TF-MoA

IPF 2013-Manufacturing Challenges for Emerging Technologies: III. Manufacturing Challenges: Electronics

Moderator: D. Seiler, National Institute of Standards and Technology (NIST), J. Hollenhorst, Agilent Technologies

2:00pm **MS+AS+EM+NS+PS+TF-MoA1 Graphene Materials and Devices Roadmap, L. Colombo, Texas Instruments** INVITED

The advancement of graphene and graphene based products will require a research and development progression similar to materials and development programs are now in full production, e.g. Si industry. The graphene research community has made significant progress over the past nearly a decade now in the physics and chemistry of graphene. We are now full engaged in the materials and device development and in some cases initial product stages. The introduction of any graphene based product will require the identification of materials, device and product metrics in order to properly keep track of the progress toward the product goals. In this presentation I will review and discuss the roadmap for various graphene based applications and present the status of materials and devices for nanoelectronic applications.

2:40pm **MS+AS+EM+NS+PS+TF-MoA3 Devices and Materials for the Post CMOS Area - What Are We Looking For?, W. Haensch, IBM T.J. Watson Research Center** INVITED

The long predicted end of scaling is coming. Many times it was predicted that the IC industry will hit a brick wall. Beginning in the early 1980's when patterning solutions were doomed to fail, then through the late 1990's when gate oxide scaling was thought to be at its end, and now in the recent years when device performance is thought to hit its physical limits. The truth is however that none of these posed an obstacle that could not be addressed. The reason while the progress of the industry enjoyed in the last several decades is slowing down is related to the ever increased power consumed to achieve ever higher performance. Seeing the end approaching, the quest for what is coming next is on! In this presentation I will give short review how we got where we are and what are the wonderful properties of MOSFET devices that allowed this extraordinary development. I will then look at the possibilities of a possible extension of the existing core logic technology. Finally I will discuss some alternate device options and provide a critical evaluation how they might fit into the IT landscape.

3:40pm **MS+AS+EM+NS+PS+TF-MoA6 Manufacturing Challenges of Directed Self-Assembly, R. Gronheid, IMEC, Belgium, P.A. Rincon Delgado, University of Chicago, T.R. Younkin, Intel Corporation, B.T. Chan, L. Van Look, I. Pollentier, IMEC, Belgium, P.F. Nealey, University of Chicago** INVITED

Directed Self-Assembly (DSA) of block copolymers (BCP) is based on nano-scale phase separation. Depending on the relative volume fraction of the blocks, different morphological structures may form in the bulk of these materials. In the case of di-block copolymers, specifically the lamellar and cylindrical phase provide structures that may be used to form line/space and hole-type patterns, respectively. When thin films of BCPs are applied on substrates that provide a pre-pattern to guide the assembly process, the orientation and direction of the resulting structures can be controlled. DSA has gained significant attention as a next method for mainstream nanofabrication in a time span of just a few years. The primary interest in the DSA technology includes the inherent variability control (since dimension is controlled through the polymer molecular weight) and the high pattern densities (typical length scales are on the order of 3-50nm) that are accessible. The outstanding questions that need to be answered in order to prove readiness of DSA for semiconductor manufacturing include defectivity, pattern transfer capabilities, pattern placement accuracy, design rule restrictions that are imposed by DSA and demonstration in an electrically functional device.

At imec, DSA based patterning has been implemented on 300mm wafers in various process flows that are compatible with semi-conductor manufacturing. These flows have been used as test vehicles to study the above-mentioned issues. In this paper, an overview will be given of the main recent accomplishments from the imec DSA program.

4:20pm **MS+AS+EM+NS+PS+TF-MoA8 Phase Change Memory, R. Bez, Micron, Italy** INVITED

Phase Change Memory (PCM) is a Non-Volatile Memory (NVM) technology that provides a set of features interesting for new applications, combining features of NVM and DRAM. PCM is at the same time a sustaining and a disruptive technology. From application point of view, PCM can be exploited by all the memory systems, especially the ones resulting from the convergence of consumer, computer and communication electronics. PCM technology relies on the ability of chalcogenide alloys, typically $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), to reversibly switch from amorphous state to poly-crystalline state. The two stable states differs for electrical resistivity, thus the information is stored in the resistance of the bit.

The alteration of the bit is possible thanks to melt-quench of the active material achieved by fast (10-100ns) electrical pulses. The energy delivered to program a bit is in the order of 10pJ, with a state of the art access time of 85ns, read throughput 266MB/s and write throughput 9MB/s. These peculiar features combined with data retention, single bit alterability, execution in place and good cycling performance enables traditional NVM utilizations but also already opened applications in LPDDR filed. Moreover PCM is considered the essential ingredient to push to the market the so called Storage-Class Memory (SCM), a non-volatile solid-state memory technology that is capable of fill the gap between CPU and disks.

In this perspective PCM technology can be effectively exploited in wireless systems, in solid state storage subsystem, in PCIe-attached storage arrays and in computing platform, exploiting the non-volatility to reduce the power consumption.

In order to be able to enter into a well established memory market there are key factors that must be fulfilled: i) match the cost of the existing technology in terms of cell size and process complexity, ii) find application opportunities optimizing the overall "memory system" and iii) provide a good perspective in terms of scalability. Phase Change Memory has been able so far to progress in line with all these requirements. Aim of this presentation is to review the PCM technology status and to discuss specific opportunities for PCM to enter in the broad memory market.

5:00pm **MS+AS+EM+NS+PS+TF-MoA10 450 mm Project, P. Farrar, University at Albany-SUNY** INVITED

The talk will focus on the leadership role the G450C consortium in driving the industry transition from 300mm to 450mm wafers. The current Status of the work at CNSE will be explored as well as the key role this public private partnership play is developing the process capability Required for High Volume Manufacturing. In addition critical success factors, and the ability to manage in a collaborative manner will be focused on.

Plasma Science and Technology

Room: 102 B - Session PS+TF-MoA

Plasma Deposition

Moderator: S. Agarwal, Colorado School of Mines

2:00pm **PS+TF-MoA1 Practical Aspects of using Tailored Voltage Waveforms for Thin Film Processing of Photovoltaic Devices, E.V. Johnson, B. Bruneau, LPICM-CNRS, Ecole Polytechnique, France, P.A. Delattre, T. Lafleur, J.-P. Booth, LPP-CNRS, Ecole Polytechnique, France**

The use of Tailored Voltage Waveforms (TVWs) to manipulate the Electrical Asymmetry Effect in a capacitively coupled plasma-enhanced chemical vapour deposition (CCPECVD) chamber has been shown to be an effective technique for device quality thin-film deposition [1,2], and a useful tool to study the interaction of the bulk and sheath properties of processing plasmas [3] and their impact on growth surfaces [4].

We have used this technique to directly study the influence of mean ion-bombardment energy (IBE) on the growth of hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) in a CCP chamber, with otherwise unchanged plasma conditions. In this work, we discuss recent results on a specific aspect of $\mu\text{-Si:H}$ growth for photovoltaic applications, the amorphous to μc phase transition. The dependence of this transition on many other parameters (power, pressure, dilution) makes the direct observation of the effect of IBE very difficult, as recently demonstrated by the efforts of other authors [5]. We instead use TVWs to vary the IBE, and in-situ ellipsometry to observe the transition in real time for a number of deposition chemistries, such as H_2/SiH_4 and $\text{Ar}/\text{H}_2/\text{SiF}_4$. Furthermore, in addition to maximizing or minimizing the IBE by changing the waveform shape, the sheath

expansion/contraction rates at the powered electrode can equally be controlled. The unexpected impact of these conditions for the $\mu\text{-Si:H}$ nucleation rate are presented, underlining the importance of "Tailoring" the waveform to the specific plasma processing goal.

Finally, we address an outstanding issue that has challenged the use of TVW's in an industrial setting – the difficulty of matching a TVW source to a CCP chamber. This has previously limited their use to only two harmonics for exciting a large area reactor at high power. We present experimental results for a prototype, high-power multifrequency matchbox that allows the effective coupling of the full output power of the amplifier to the PECVD chamber, enabling high deposition rate $\mu\text{-Si:H}$. These increased deposition rates, along with in-situ observation of the film evolution during growth, will be shown.

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[2] D. Hrunski, *et al*, *Vacuum* **87** (2013) 114.

[3] T. Lafleur, P.A. Delattre, E.V. Johnson, and J.P. Booth. *Appl. Phys. Lett.* **101**, (2012)124104.

[4] E.V. Johnson, S. Pouliquen, P-A. Delattre, and J.P. Booth, *J. Non-Cryst. Solids* **358**. (2012), 1974.

[5] A. C. Bronneberg, N. Cankoy, M. C. M. van de Sanden, and M. Creatore, *J. Vac. Sci. Technol.* **A30**, 061512 (2012).

2:20pm PS+TF-MoA2 Characteristics of Plasma Generated by ICP-CVD with Various H_2/SiH_4 Ratios and the Resultant Properties of nc-Si:H Thin Films, *J.H. Hsieh, Y.L. Lie, S.C. Lin*, Ming Chi University of Technology, Taiwan, Republic of China

nc-Si:H thin films were deposited with an ICP-CVD system attached with four internal antennas, under the variation of H_2/SiH_4 ratios (R). During deposition, the generated plasma was characterized using a Langmuir probe and an optical emission spectrometer (OES). The films' properties were characterized using Raman spectrometry and FTIR. The results were correlated with those obtained from probe and OES studies. It was found that the crystallinity of nc-Si:H film was significantly affected by plasma density which was increased with the increase of R, but only to a certain extent. Both the plasma density and Xc reached the maximum at R=10, then leveled off. The deposition rate decreased with the increase of IHa* which is obtained from the OES results. Also, it was also found that the crystallinity could be proportionally related to the increase of $I^*(\text{SiH}_2+\text{SiH}_3)/I(\text{SiH}+\text{SiH}_2+\text{SiH}_3)$ in FTIR spectra. This is could be due to that di-/poly- hydride bonding could serve to passivate the grain boundaries of Si nano-crystalline clusters.

2:40pm PS+TF-MoA3 Medium Range Order (MRO) in "Amorphous (a)-Si(H)" Alloys in PV and TFT Devices with Intrinsic, B and P Doped a-Si(H) and a-Si,Ge(H) Layers: Reduction of Photo- and Stress-induced Defects by O-bonding, *G. Lucovsky, D. Zeller, C. Cheng, Y. Zhang*, North Carolina State University

INVITED

Intrinsic photo-absorbing regions, and B and P doped contacts comprised of hydrogenated amorphous silicon, a-Si_{1-x}H_x, with ~10 at.% or x ~0.1±0.02, are used in photovoltaic devices (PV), and thin film transistors (TFT's). A-Si thin films, assumed to be free of H, are used as precursors for polycrystalline gate electrodes in microelectronics. Intrinsic, and p-type and n-type layers in multi-layer stacks that include "a-Si,Ge(H)" have been assumed to be "amorphous continuous random networks (CRN)", with limited short range order (SRO) extending to 1st nearest neighbor (NN) bond lengths, and 2nd N-N bond-angles. A-Si(H) films are not CRNs. They have medium range order (MRO) extending to self-organized and symmetry determined dihedral angles. MRO and formation of non-periodic organized nm-scale ordered regions with crystalline-Si symmetries is responsible for enabling properties in a-Si(H) devices. Intrinsic a-Si(H) thin films have been deposited by glow discharge (GD), remote plasma-enhanced chemical vapor deposition (RPECVD), and reactive magnetron sputtering (RMS). The concentrations of bonded-H are determined by deposition precursors and substrate temperatures. Two conditions are necessary for low Si dangling bond densities to ~0.5 to 1x10¹⁶ cm⁻³: (i) a bonded mono-hydride, Si-H, concentration of ~10 at.% H, and (ii) a deposition, and/or a post-deposition anneal at ~240°C to 300°C [1]. These combine to reduce strain-induced defects by introducing MRO as 1 nm-ordered clusters. Si L_{2,3} X-ray absorption spectroscopy (XAS) confirms MRO by yielding non-vanishing ligand-field splittings (DLF) of e_g and t_{2g} atomic d-states. The MRO basis states are symmetry-adapted linear combinations (SALC) of atomic states and form molecular orbital valence bands. MRO symmetry promotes a H-atom transfer reaction from a the Si-H bond at the apex of the MRO cluster into a Si-H-Si bonds at NN sites. This reaction establishes the low level of dangling bond defect sites. The same H-atom transfer is induced by sunlight absorption in PV devices. This increase dangling bond concentrations is the Staebler-Wronski effect (SWE). The local bonding arrangements of P

and B dopant atoms are qualitatively different. If the bonding sites were the same as substitutional sites in c-Si, each of these dopants would be 4-fold coordinated. The incorporation of P is the same as in crystalline Si, 4-fold coordinated, and the ionization energy of the P⁺ site is small giving rise to a high doping efficiency, i.e., in electrons/P atom [2]. B is 3-fold coordinated, and p-orbitals perpendicular to the 3-fold coordinated bonding plane act as an electron acceptor creating hole transport.

Each of the preferred bonding arrangements for P- and B-atoms includes remote induction stabilized Si-H reducing Si-atom dangling bond densities. This accounts for a reduction of the E' center signal strength in electron spin resonance (ESR) measurements. Finally, the local bonding of 2-fold coordinated O-atoms, and 3-fold coordinated N-atoms have similar effects as 1-fold coordinated H-atoms, introducing new MRO local bonding arrangements. When combined with 1-fold coordinated NN Si-H bonds, the 2- and 3-fold local symmetries introduce coupled mode motions that stabilize unique MRO clusters by increasing their total binding energy. This stabilization provides a reduction in the Staebler-Wronski Effect photo-degradation in PV devices by process-controlled low densities (<10¹⁸ cm⁻³) of plasma processing incorporation of O- and N-atoms and coupled O-H/H-H bonds.

Similar reductions reduce electron trapping in TFTs.

1. G. Lucovsky and F.L. Galeener, *J. of Non-Cryst. Solids* **35 & 36** (1980) 1209.

2. G.N. Parsons, C. Wang and M.J. Williams, *Appl. Phys. Lett.* **56**, 1985 (1990).

3. D.E. Steabler and C.R. Wronski, *J. Appl. Phys.* **51** (6), (1980) 3262.

3:40pm PS+TF-MoA6 Plasma Prize Talk - Plasma Processing Advances at Illinois, *D.N. Ruzic*, University of Illinois at Urbana Champaign

INVITED

Recent advances in plasma processing at Illinois will be discussed. The first is the investigation of high-powered pulsed magnetron sputtering (HiPIMS) by creating a hole in the target racetrack and placing a gridded energy analyzer and quartz-crystal monitor (QCM) behind it. In this way the metal ion and Ar ion flux can be measured, as well as the neutral metal atom flux. These measurements show the true mechanism behind the high surge in current during a HiPIMS pulse. The next subject is creating PVD-like coatings at atmospheric pressure. This is done by introducing atoms of the coating material directly into the plasma plume of an atmospheric-pressure torch either through laser ablation or by evaporation. These coatings have many industrial applications and since they can be made in the field instead of inside a vacuum chamber, their utility is increased and their cost reduced. Lastly, the use of a metal-surface-wave plasma source will be described. Low-damage crystalline and amorphous silicon can be produced with it leading to higher-efficiency solar cells and other applications.

4:20pm PS+TF-MoA8 PECVD, Rf vs Dual Frequency : Investigation of Plasma Influence on Metalorganic Precursors Decomposition and Material Characteristics, *F. Pierrat*, STMicroelectronics, France, *C. Vallee*, Ltm - Minatec - Cea/leti, France, *R. Gassilloud*, *P. Michallon*, CEA-LETI, France, *B. Pelissier*, Ltm - Minatec - Cea/leti, France, *P. Caubet*, STMicroelectronics, France

In the last decade, Dual Frequency (DF) reactors have been considerably developed as fine etching tool for microelectronic manufacturing. In this case, the CCP source is driven by a high frequency (HF) and a LF sources attached on either one electrode or two electrodes separately. Usually one frequency is chosen to be much higher than the other in order to achieve an independent control of ion bombardment and electron density (i.e. ion flux). In the case of deposition process, it has been observed for Silicon Nitride deposition that the HF to LF ratio in the plasma modify the ion flux and energy and so the mechanical properties of the material [3]. Moreover, addition of LF to HF can modify the sheath thickness of the plasma and so increase the electron temperature of the gas [4]. In this way, the precursor fragmentation can be tuned by tuning the LF power what will impact the deposition rate and thin film properties.

In this study we compare RF and Dual frequency deposition of materials for metal gate applications such as TiCN and TaCN. The reactor used is a 300 mm Metal Organic PECVD industrial tool in which the plasma is sustained capacitively by a RF power supply (13.56 MHz) and a LF (350 kHz) source. Impact of LF addition on the metal composition and its physical properties is analyzed and correlated to plasma modification observed by OES (Optical Emission Spectroscopy). For both metalorganic precursors we observe a strong modification of the metal properties and deposition rate when adding 25 to 100 W LF to a 200 W RF plasma. As an example, in case of TiN, with 50 W LF added to a 200 W RF, the deposition rate increased more than twice, the film appears to be less resistive (50%) and denser. These modifications highlight the change of deposition mechanisms/reactions. The beneficial effect of adding a weak LF power to

the RF power can be correlated to a modification of the precursor fragmentation as observed by OES. These results are less pronounced and not obtained when only RF plasma is used, whatever the increasing power (from 200 to 300 W). Finally, with LF addition, we also hope, to reduce the RF plasma impact on the dielectric leading to a regrowth of Equivalent Oxide Thickness (EOT) observed previously in our p-like metal MOS capacitors [5].

- [1] H. N. Alshareef *et al*, Electrochemical and Solid-State Letters **11** (2008) H18
- [2] H. Zhu *et al*, Phys. Review B **80** (2009) 201406
- [3] W.S. Tan *et al*, Journal of Electronic Materials **33** (2004) 400-407
- [4] W-J Huang *et al*, Phys. Plasmas **16** (2009) 043509
- [5] F. Piallat *et al*, AVS 59th Tampa (Florida, USA)

4:40pm **PS+TF-MoA9 Reactive High Power Impulse Magnetron Sputtering (HiPIMS), J.T. Gudmundsson**, University of Iceland, F. Magnus, Uppsala University, Sweden, T.K. Tryggvason, S. Shayestehaminzadeh, S. Olafsson, University of Iceland

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of a high dissociation fraction of the molecular gas. Here we discuss reactive high power impulse magnetron sputtering (HiPIMS) of Ti target in Ar/N₂ and Ar/O₂ atmosphere. The discharge current waveform is highly dependent on the reactive gas flowrate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [2] or oxide [3] forms on the target. We also discuss the growth of TiN films on SiO₂ at temperatures of 22-600 °C. The HiPIMS process produces denser films at lower growth temperature and the surface is much smoother and have a significantly lower resistivity than dc magnetron sputtered films on SiO₂ at all growth temperatures due to reduced grain boundary scattering [4,5].

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- [2] F. Magnus, O. B. Sveinsson, S. Olafsson and J. T. Gudmundsson, J. Appl. Phys., **110** 083306 (2011)
- [3] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, J. Vac. Sci. Technol., **30** (2012) 050601
- [4] F. Magnus, A. S. Ingason, S. Olafsson and J. T. Gudmundsson, IEEE Elec. Dev. Lett., **33** (2012) 1045 - 1047
- [5] S. Shayestehaminzadeh, T. K. Tryggvason, L. Karlsson, S. Olafsson and J. T. Gudmundsson, Thin Solid Films, submitted 2012

5:00pm **PS+TF-MoA10 Sputtering Yields and Selectivity of Magnetic Materials by Chemically Reactive Plasmas, H. Li, Y. Muraki, K. Karahashi, S. Hamaguchi**, Osaka University, Japan

Based on highly developed reactive ion etching (RIE) technologies, micro-fabrication of Si-based semiconductor devices has been considerably developed for the last few decades. However, as non-conventional micro devices, such as magnetic random access memory (MRAM) devices, have been developed recently, there has been a considerable demand for RIE processes of non-conventional materials such as magnetic materials with nonconventional gases such as CO/NH₃ and methanol. In this study, we examine sputtering yields and surface reaction characteristics for MRAM etching by CO/NH₃ or methanol plasmas. Especially we focus on effects of oxygen and nitrogen in incident ions that are likely to induce selectivity of magnetic materials over Ta, i.e., a widely used mask material in such processes. In this study, we use a multi-beam system (i.e., mass-selected ion beam system), which allows only selected ions with specified energy to be injected into a sample substrate set in an ultra-high-vacuum (UHV) chamber. Using the beam system, rather than an actual plasma etching system, we can examine specific surface reactions caused by a specific combination of a sample material and incident ions (and/or radicals). In the beam system, chemical surface compositions are analyzed by *in-situ* XPS. In this study, the incident ion energy and angle of incidence were varied from 300eV to 1000eV and from 0° to 75°. The sputtering yields were measured as functions of energy and/or angle of incidence for various materials including Ni, Fe, Co, Ta, and TaO_x. It has been found that, in most cases, etching processes for these materials are nearly of physical sputtering. For simple physical sputtering (by, e.g., Ar⁺ ions), the sputtering yield of Ta is much lower than the magnetic materials (Ni, Co, Fe), which justifies the use of Ta as a mask material. Furthermore, from XPS spectrum observation, it has been found that, when N or O are in the incident ionic species, Ta form a nitride or an oxide and its sputtering yield becomes even lower. These results have confirmed that, in CO/NH₃ or methanol plasma etching processes of magnetic materials with Ta masks, the observed selectivity is essentially caused by the formation of hard-to-etch oxides

and/or nitrides of masks, rather than enhanced etching yields of magnetic materials by these plasmas.

5:20pm **PS+TF-MoA11 Two-dimensional Growth of Novel ZnO based Semiconductor ZnInON with Tunable Bandgap by Magnetron Sputtering, K. Matsushima, R. Shimizu, D. Yamashita, G. Uchida, H. Seo, K. Kamataki, K. Koga, M. Shiratani, N. Itagaki**, Kyushu University, Japan

Materials with tunable bandgap are required for optoelectronics applications such as photo detectors, solar cells, light emitting diodes, and so on. Recently we have developed a novel ZnO based semiconductor, ZnInON (ZION), with tunable bandgap from 1.6 eV to 3.3 eV, being fabricated by sputtering method [1]. ZION has wurtzite crystal structure and high absorption coefficient of 10⁵ cm⁻¹. Here we have studied effects of Ar partial pressure during the sputtering deposition on the crystal growth of ZION films by means of plasma parameter measurements and evaluation of film properties such as crystallinity and electrical properties. Furthermore, we have demonstrated two-dimensional growth of single crystalline ZION films.

First, 10-nm-thick ZnO buffer layers were fabricated on c-Al₂O₃ substrates via nitrogen mediated crystallization (NMC) in N₂-Ar atmosphere at 700°C [2]. Then, 1-μm-thick ZnO templates were fabricated on the ZnO buffer layers by RF magnetron sputtering at 700°C in Ar-O₂ atmosphere. Finally, epitaxial ZION films were fabricated on the ZnO templates by RF magnetron sputtering. For fabrication of ZION films, N₂, O₂ and Ar gases were used. The total pressure was 0.28 Pa and the partial pressure of Ar was 0.04-0.17 Pa. The supplied RF power was 0.49-3.95 W/cm² and the deposition temperature was 360°C. The ZION film thickness was 30-50 nm.

X-ray diffraction measurements show that the full width at half maximum (FWHM) of rocking curves from (002) plane for the ZION films are noticeably small of 0.09°, being independent of the partial pressure of Ar in the sputtering atmosphere. Hall-effect measurements using the Van Der Pauw configuration reveal that the carrier density of ZION films decreases from 1.1×10²⁰ cm⁻³ to 3.7×10¹⁹ cm⁻³ and the electron mobility increases from 66 cm²/Vsec to 87 cm²/Vsec with decreasing the partial pressure of Ar from 0.17 Pa to 0.04 Pa. This is because electron temperature in the plasma increases with decreasing the partial pressure of Ar, and thus the dissociation of oxygen and nitrogen molecules is enhanced, which can suppress the lattice defects related to nitrogen and/or oxygen deficiencies. Moreover, two-dimensional crystal growth of ZION films was observed at a low Ar partial pressure of 0.04 Pa. These results show that Ar partial pressure in sputtering atmosphere is an important parameter to control the growth mode and to improve electrical properties of ZION films.

This work was partially supported by JSPS and PRESTO.

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Plasma Science and Technology Room: 104 C - Session PS-MoA

Advanced BEOL/Interconnect Etching

Moderator: S. Hamaguchi, Osaka University, Japan

2:00pm **PS-MoA1 Etching Challenges in the BEOL for sub 20nm Technology Nodes, K. Kumar, Y.P. Feuprier, L. Wang, J. Stillahn, Y. Chiba, A. Ranjan, A. Metz, A. Ko, D.M. Morvay, A. Selino, P. Biolsi**, TEL Technology Center, America, LLC

INVITED

In the sub-32nm technology node, Trench First Metal Hard Mask (TFMHM) integration scheme has gained traction and become the preferred integration of low-k materials for BEOL. This integration scheme also enables Self-Aligned Via (SAV) patterning which prevents via CD growth and confines via by line trenches to better control via to line spacing. In addition to this, lack of scaling of 193nm Lithography and non-availability of EUV based lithography beyond concept, has placed focus on novel multiple patterning schemes. This added complexity has resulted in multiple etch schemes to enable technology scaling below 80nm Pitches, as shown by the memory manufacturers. Double-Patterning and Quad-Patterning have become increasingly used techniques to achieve 64nm, 56nm and 45nm Pitch technologies in Back-end-of-the-line. Challenges associated in the plasma etching of these integration schemes, along with the challenges posed with etching EUV resists, in concert with shape formation of the dual-damascene will be discussed in the presentation.

2:40pm **PS-MoA3 Plasma Etch Challenges at 10nm and beyond Technology Nodes using Multi Patterning Techniques in the BEOL to Produce Metallization-Friendly Profiles**, *Y. Mignot*, STMicroelectronics, *M. Beard, B.G. Morris, B. Peethala, IBM, Y. Loquet*, STMicroelectronics, *J.H. Chen, IBM, S. Nam*, GLOBALFOUNDRIES U.S. Inc., *B. Nagabhirava, P. Friddle*, Lam Research Corp

As feature critical dimension (CD) shrinks towards and beyond the 48nm pitch, new patterning techniques within the context of a trench-first-metal-hard-mask (TFMHM) patterning scheme have been developed to generate trenches and vias below 48nm pitch. One of the main challenges at advanced nodes is to create structures (i.e., trenches & vias) that can be robustly metallized. This requires several elements of focus for the etches: first, there must be zero dielectric etch damage that results in undercut of any hard masks in the film stack; second, the aspect ratio of the final etch structure must be minimized; and third, the shape of the trench or via profile must be tailored to be metallization-friendly (i.e., slight angle better than vertical) and finally a good selectivity on lower metallization in case of wet HMO faceting. These requirements often conflict with each other, especially within a patterning scheme that requires self-aligned vias, where the desired high selectivity to the hard mask conflicts with the need to minimize the amount of hard mask left in order to decrease aspect ratio. In this paper, we will discuss some of the approaches that we have investigated to achieve the best profile for metallization. This includes plasma etch all-in-one (AIO) dielectric etch optimization as well as multi-step solutions that potentially can use techniques including wet chemistries plus dry faceting and dry metal HMO removal. In addition, data will present an overview of the multi-patterning techniques such as multiple Litho-Etch (LE3), Sidewall Image transfer (SIT) and double patterning for self aligned via (DPSAV) to expose and understand the multiple underlying interactions at Dielectric RIE such as the SIT Block Mask with the DPSAV features.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities

3:40pm **PS-MoA6 Fine Patterning of Copper by Plasma Etch Process for Advanced BEOL Interconnects**, *H. Miyazoe*, IBM T.J. Watson Research Center, *M. Hoinkis*, Applied Materials Inc., *B.N. To, G. Fritz, A. Pyzyna, M. Brink, C. Cabral*, IBM T.J. Watson Research Center, *C. Yan, I. Ne'emam*, Applied Materials Inc., *E.A. Joseph*, IBM T.J. Watson Research Center

As device scaling continues beyond the 10 nm node, challenges in back end of line (BEOL) interconnect technology continue to multiply. Expanding beyond the known issues of patterning and integration of porous ultra low-k (ULK) materials, new issues such as line edge roughness and line width roughness (LER/LWR) as well as increased resistivity (emanating from grain boundary scattering) are only compounding the difficulties at hand and may require significant modifications to the typical damascene integration flow. Subtractive etching of Cu has a potential to overcome current difficulties in interconnects integration such as the increase of resistivity caused by electron scattering at grain boundary, poor coverage of liner/seed materials, and a time dependent dielectric breakthrough (TDDB) issue of ULK material by starting from blanket Cu film with large crystal (>1 μ m), by depositing it directly on Cu patterns, and by minimizing plasma damage during ULK etch, respectively. In this work, we examine one such alternative approach to conventional dual damascene copper integration, in which subtractive patterning of copper is employed. Successful patterning of copper at smaller than 50 nm critical dimension (CD) with smaller than 100nm in pitch is demonstrated using a novel high density plasma based dry etch process. Consisting of a reactive sputter based etch chemistry, appreciable etch rates on the order of ~15Å/s are achieved, with high selectivity (>6:1) to masking layers. The angle of sidewall of approximately 85° was achieved at an optimized condition while we obtained ~45° in case of physical sputtering using pure Ar plasma. We confirmed that the resistivity of fabricate Cu line increases with the decrease of line CD. The resistivity of isolated Cu line at CD of ~30 nm is ranging from 10 to 20 μ ohm cm. A full review of the etch process, its mechanism and the positive implications on ULK materials, LER and LWR, metal resistivity and overall reliability will be discussed in detail.

4:00pm **PS-MoA7 Virtual Fabrication for BEOL Module Optimization Beyond the 22nm Technology Node**, *R. Patz, D. Fried, K. Greiner, M. Stock, D. Faken, J. Lehto, A. Pap, B. van Dyk, M. Kamon, S. Breit*, Coventor, Inc.

Virtual fabrication provides a powerful platform for exploring process interactions in 3D, reducing time-consuming and costly trial-and-error silicon experimentation. A Trench First Metal Hard Mask BEOL integration scheme including Self-Aligned Vias (TFMHM-SAV) has been characterized using a M1-V1-M2 example. Experiments focused on the patterning operations involved, and were based on 64nm Mx pitch designs. Variation studies were used to determine the key drivers of V1-M1 contact area, liner coverage and via spacing. A full-wafer study showed the impact

of patterning and deposition non-uniformity. This full-wafer virtual fabrication data can focus attention on the most critical unit processes and enable Automated Process Control (APC).

V1-M1 contact area, a critical electrical and reliability criterion, was primarily determined in this integration scheme by M1 lithography bias. Through a +/- 3nm range of M1 exposure, the contact area varied more than 3x, from 322nm² to 1091nm². Chamfer profile, critical for electromigration reliability, was dictated by the Mx Overetch (OE) depth and sputter ratio (ion energy). Cross-sectional analysis was used to characterize the final metallization, enabling conclusions regarding resistance and yield. TiN selectivity during the M2 etch dominated the profile, leading to metallization differences. Surprisingly, the cross-sectional area of Mx copper decreased slightly (~3%) with reduced TiN selectivity (from 40:1 to 10:1), a change that opened the top profile and was expected to lead to improved copper fill. 3D model inspection revealed that this effect was driven by a "shoulder" in the cap layer, resulting in a metallization profile degrade.

Geometries beyond the 22nm technology node and resulting unit process requirements push the limits of process tool capability and cross-wafer uniformity. A module-level approach must be considered to compensate for uniformity limitations of any single process by adjusting specifications elsewhere in the process flow. A full-wafer virtual fabrication experiment explored cross-wafer deposition and patterning variation in the M1-V1-M2 module to quantify the aggregate effect of many realistic unit process steps on the fully-integrated structure. While these cross-wafer variations yielded a 1sigma uniformity of 12% in Mx copper cross-sectional area, the sensitivities lay the foundation for APC-based yield improvement.

4:20pm **PS-MoA8 Improvements in Low-k Damage and Hard Mask Selectivity in BEOL Dielectric Etch Using C5HF7**, *R.L. Bruce*, IBM T.J. Watson Research Center, *T. Suzuki, M. Nakamura*, Zeon Chemicals LP, *S.U. Engelmann, E.A. Joseph, N. Fuller, E.M. Sikorski*, IBM T.J. Watson Research Center, *A. Itou*, Zeon Corporation

As feature sizes continue to decrease, significant issues are found using highly selective fluorocarbon gases to etch interconnect low-k dielectrics. Three examples of these challenges include; line wiggling, low-k damage, and low selectivity (e.g. to organic masks). To address these challenging issues, we have evaluated C5HF7 and other novel etch gases for 14nm and 22nm devices to determine if they enable the optimized fabrication of BEOL interconnects. Etch performance is assessed for both trench and via patterns and also when incorporated into full dual-damascene structures. Compared to conventional fluorocarbon etch gases such as C4F6 and CF4/CHF3 mixtures, experiments with C5HF7 have shown a substantial increase in low-k dielectric to metal hard mask and capping layer selectivity for trench and self-aligned via etching. Low-k damage is also investigated by post-etch HF treatment to measure critical dimension loss from dissolution of plasma-damaged dielectric. A significant reduction in damage is observed with C5HF7 in low-k films of two different dielectric constants. Finally, we propose a mechanism for high selectivity, low damage dielectric etch at sub-80nm pitch structures using rationally-designed novel etch gases.

4:40pm **PS-MoA9 Mitigation of Plasma-induced Damage of Advanced 2.0 Porous Dielectrics by the Pore Stuffing Approach**, *M.H. Heyne, L. Zhang*, KU Leuven, Belgium, *J.-F. De Marneffe, R. Gronheid, C.J. Wilson, M. Baklanov*, IMEC, Belgium

Plasma-induced damage is a major hurdle for the integration of 2.0 dielectrics in advanced interconnects targeting sub-10 nm nodes. State-of-the-art low-k dielectrics are porous organo-silicate glass (p-OSG) films, with high carbon content and interconnected porosities up to 50 %, making the material sensitive to modifications by plasma reactive radicals and VUV photons. A possible solution is the so-called pore stuffing approach: after porogen burnout, a sacrificial polymer is introduced into the porous matrix, hampering diffusion of radicals in the bulk material and attenuating VUV light propagation.

PECVD ultra-low-k dielectric films with k = 2.0 and porosity of 40 – 50 % were stuffed with PMMA. The protection efficiency was evaluated against fluorocarbon-based, oxygen-based plasmas and 147 nm VUV light generated in industrially relevant 300 mm CCP chambers. The material damage was determined by FTIR, spectroscopic ellipsometry, ellipsometric porosimetry, TOF-SIMS, water contact angle measurements, and capacitance measurements. Plasma damage was significantly reduced in PMMA protected samples, resulting in lower hydrophilicity, smaller carbon loss, smaller fluorine penetration, and lower dielectric constants in comparison to unprotected material. PMMAs of molecular weights between 2000 and 7000 g/mol influenced the filling conditions and filling process window, but gave similar level of plasma protection. Plasma-induced VUV light led to significant PMMA degradation, through carbonyl bonds depletion and formation of other polymer by-products, resulting in only a

short-term protection of the dielectric against 147 nm radiation. Pattern transfer for 40 nm lines required small changes in discharge parameters, and resulted in lowered sidewall damage when compared to non-stuffed samples.

After the etching, the polymer is usually removed from the pores by a thermal burn-out above 400°C, which is not compatible with BEOL processing. An alternative approach is proposed, using a non-damaging He/H₂ downstream plasma at 280°C, allowing a full CMOS process compatibility.

Pore stuffing is a promising approach to mitigate the plasma damage in porous ultra-low-k material by using a temporary hybrid material approach. In contrast to former hybrid solutions, this one is not suffering from shrinkage or material interaction and therefore, might allow one further step to $k_{\text{eff}} \leq 2.0$ interconnect systems.

5:00pm **PS-MoA10 EPR Studies of SiOC:H BEOL (Low-k) Dielectrics**, T.A. Pomorski, P.M. Lenahan, M. Mutch, Penn State University, S.W. King, Intel Corporation

Low- κ interlayer dielectrics with dielectric constants significantly less than those of SiO₂ and are utilized to reduce capacitance induced RC delays in ULSI circuits. [1,2] At the present time, very little is known about the underlying physical mechanisms involved in electronic transport within these films. Recent electron paramagnetic resonance (EPR) studies have reported on defect centers in some of these films [3,4]. In one study, comparisons were made between EPR defect densities and leakage currents before and after exposure to UV light under conditions generally similar to those during industrial UV curing. That study noted that large UV induced changes in spin density were accompanied by large changes in dielectric leakage, suggesting a link between the defects and leakage.[3] In this study we have conducted a considerable more extensive survey specifically focused upon low- κ SiOC:H films. We find that a large variety of paramagnetic centers are present in the dielectrics and that both the types of defects present and the defect densities are quite strong functions of processing parameters. Defects include silicon dangling bond centers in which the silicon is back bonded to three oxygens (E' centers), silicon dangling bond centers complexed to a single hydrogen atom, a dangling bond center complexed to three equivalent hydrogens, and very likely carbon dangling bond centers. In, limited cross section of samples, all with the EPR dominated by a center with a zero crossing $g=2.0026 \pm 0.0003$ and all similarly processed, we observe strong correlation between defect density and dielectric leakage currents. It should be noted that quite recent SiOC:H studies which have utilized another analytical approach has also identified the presence of E' centers in similar films. King et. al. recently reported on reflection electron energy loss spectrometry (REELS) on similar dielectric films and noted the presence of REELS spectra consistent with E' centers a result which our EPR data supports.[5]

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[2] W. Volksen, R.D. Miller, and G. Dubois, *Chem Rev.* **110**, 56 (2010).

[3] B. Bittel, P. Lenahan, S. King, *Appl. Phys. Lett.* **97**, 6 (2010)

[4] H. Ren, et. al. *Appl. Phys. Lett.* **98**, 10 (2011)

[5] S.W. King, B. French, E. Mays, *J. Appl. Phys.*, 113, 044109 (2013)

5:20pm **PS-MoA11 Effect of NH₃/N₂ Ratio in Plasma Treatment on Porous Low Dielectric Constant SiCOH Dielectric**, Y.L. Cheng, J.F. Huang, T.C. Bo, National Chi-Nan University, Taiwan, Republic of China

The influence of N₂/NH₃ ratio in the plasma treatment on physical, electrical properties and reliability characteristics is investigated in this study. It is found that all the plasma treatments resulted in the formation of a thin and modified layer on the surface of the porous low- κ films, and the properties of this modified layer is affected by N₂/NH₃ ratio in the plasma. Results indicate that pure N₂ plasma treatment forms an amide-like layer on the surface, which apparently leads to a higher increase in the dielectric constant. A mixture of N₂/NH₃ gas plasma treatment induces more moisture uptake on the low- κ dielectric's surface, which degrade the electrical performance and reliability. Among N₂/NH₃ gas plasma treatment, plasma-treated low- κ dielectric has better electrical and reliability characteristics as N₂/NH₃ gas ratio equals to 1.

Electronic Materials and Processing
Room: 101 B - Session EM+PS-TuM

High-k Oxides for MOSFETs and Memory Devices I

Moderator: A.C. Kummel, University of California San Diego

8:00am **EM+PS-TuM1 Calibration of Capacitance Force Microscopy using Micro-scale Gold Dots**, *K. Sardashti, A.C. Kummel*, University of California San Diego

Capacitance force microscopy (CFM) is a variant of atomic force microscopy (AFM) and a powerful tool in characterization of metal-oxide-semiconductor capacitors (MOSCAPs). A high accuracy CFM system can be built by modifying a commercially available AFM, connecting the tip and sample to capacitance bridge of tunable frequency. The electric field distribution and, as a result, minority carriers' response to the applied bias strongly depend on the contact area between the gate and oxide. Furthermore, the frequency dependence of the capacitance-voltage measurement (C-V) is a function of the electrode size due to the radial diffusion of minority carriers near the periphery of the electrode as the dimension shrinks to the size of AFM tips. Therefore, contact area between the tip and sample is a crucial factor in CFM measurements. An experimental method is required to determine the effect of contact area on the shape and frequency-dependence of C-V curves measured by CFM. Scanning capacitance calibration samples are being fabricated with gold dots of diameters ranging from 2 to 600 μm on heavily doped silicon with 100 nm thick SiO_2 grown on top. The capacitance of resulting $\text{Au/SiO}_2/\text{Si}^-$ stacks with a 90000x range of area will be measured both by a conventional probe station (Agilent B-1500) and a CFM system (Veeco Multimode[®] connected to an AH 2700A capacitance bridge). After calibration, second set of samples including gold dots of similar size on Al_2O_3 layers, grown by atomic layer deposition (ALD), on GaN substrates will be characterized by both the probe station and CFM systems.

8:20am **EM+PS-TuM2 RF-PVD Si Capping for CET Decrease in High-k/Metal Gate 14nm FDSOI**, *C. Suarez Segovia, P. Caubet*, STMicroelectronics, France, *C. Leroux*, CEA-LETI, France, *M. Juhel, S. Zoll, O. Weber*, STMicroelectronics, France, *G. Ghibaudo*, IMEP-LAHC, France

Further miniaturization of CMOS technologies will require low values for Capacitance Equivalent Thickness (CET) of gate dielectrics. Below 28nm node, it becomes more difficult for high-k/metal gate (HKMG) MOSFET to reach low CET without degrading gate leakage. One technique for CET scaling already reported [1-4] is based on oxygen scavenging from the HKMG stack after thermal treatment (drive-in anneal). Unlike other reported CET scaling solutions, oxygen scavenging is a promising approach to extend HF-based HK dielectrics to future nodes [2].

Scavenging techniques incorporating the scavenging elements such as Hf, La, Ti, Al, and Ta directly within the high-k layers have been proposed by many researchers [2-3]. However, this approach can present several drawbacks such as excessive carrier mobility degradation, leakage current increase and effective work function change by formation of fixed charges and/or interface dipoles [3].

In this study, in-situ RF-PVD Si-cap was deposited on top of metal gate in an Applied Materials Endura chamber. HfO_2 and TiN metal gate were used on 300mm FDSOI wafers, using a gate-first integration scheme in a 14nm process flow. The use of an in-situ Si-cap for achieving CET reduction has already been reported in the literature [4]; but, for the first time in this article, we have evaluated a new RF mode PVD Si-cap process, designed to avoid device degradation due to charging.

Firstly, SIMS and XRD measurements were carried out on blanket wafers containing either 20Å or 100Å thick RF-PVD Si-cap deposited in-situ on sacrificial 35Å TiN layer followed or not by drive-in anneal. SIMS results show that amorphous silicon is oxidized at TiN/Si-cap interface during drive-in anneal by pumping oxygen from TiN and high-k, which reduces CET. We demonstrate that Si-cap deposited by RF-PVD remains amorphous for both studied thicknesses whereas sacrificial 35Å TiN layer crystallizes after drive-in anneal, as indicated by XRD. We believe that oxygen diffusion through TiN is possible by means of the grain boundaries formed in TiN during annealing. Secondly, electrical measurements were obtained on 14nm FDSOI devices. As expected, with TiN capping by RF-PVD Si, we succeed to reduce CET by 1Å (6.25%) in PMOS and 0.5Å (4%) in NMOS with no significant degradation of the gate current leakage, no measurable impact on VT, and no device degradation due to charging.

[1] T. Ando et al., Proceedings of IEEE IEDM, Washington, DC, USA 2009; pp. 423-426

[2] Takashi Ando, Materials 2012, 5, 478-500

[3] C. Choi et al J. Appl. Phys. 2010, 108, 064107:1-064107:4

[4] L.-Å. Ragnarsson et al, Proceedings of IEEE IEDM, Baltimore, MA, USA 2009; pp. 663-666

8:40am **EM+PS-TuM3 Growth of Oxides for Negative Capacitance Gate Dielectrics**, *R. Droopad*, Texas State University **INVITED**

The need to reduce power in CMOS devices is critical to the evolution of the next generation devices as scaling continues. The use of new materials for the gate dielectric, and with the possibility of using III-V semiconductors in the channel, there is additional new challenges to maintaining high on-off ratios. One way to reducing the subthreshold slope in low power MOSFET application is through the use of the negative capacitance of ferroelectric layers as part of the gate dielectric proposed by Salahuddin and Datta [1]. This concept has been demonstrated in a polymer ferroelectric MOSFET device exhibiting a sub-60 mV/decade switching behavior [2]. Capacitance enhancement in crystalline ferroelectric-dielectric bilayer has also been demonstrated using a PZT-STO bilayer [3]. Unlike the present amorphous gate stack, ferroelectric gate materials need to be crystalline for the realization of polarization that is oriented along the growth direction. This presentation will detail the growth of ferroelectric complex oxide gate stacks epitaxially on both Si and III-V heterostructures. Deposition is carried out using MBE with careful control of the interfacial nucleation ensuring that the ferroelectric polarization is in the growth direction.

[1] S. Salahuddin, S. Datta, Nanolett. 8 (2008) 405.

[2] A. Rusu, G.A. Salvatore, D. Jiménez, A.M. Ionescu, IEDM 2010

[3] A.I. Khan, D. Bhowmik, P. Yu, S. J. Kim, X. Q. Pan, R. Ramesh, S. Salahuddin, Appl. Phys. Letts., 99 (2011) 113501

9:20am **EM+PS-TuM5 Switching Aspects of RRAM – First Principles and Model Simulations Insight**, *S. Clima, R. Degraeve, K. Sankaran, Y.Y. Chen, A. Fantini, A. Belmonte, L. Zhang, N. Raghavan, L. Goux, B. Govoreanu, D.J. Wouters, M. Jurczak, G. Pourtois*, IMEC, Belgium **INVITED**

The Resistive Random Access Memory with its great potential for scalability to the nanoscale dimensions, high speed, low energy switching and CMOS compatibility, is emerging as a promising candidate for non-volatile memories.¹⁻⁴ Having a good understanding of the mechanisms at the origin of the switching at the atomic level is important for designing high performance resistive memory stack. For instance, the thermodynamic driving forces that help shaping a suitable oxygen profile for low forming voltages might prove to be disadvantageous for a good endurance. Another trade-off that needs further considerations is the compromise between the retention and the switching dynamics, determined by the kinetic energy barriers of the conducting defect. With the help of classical DFT and bond-booster Accelerated Ab Initio Molecular Dynamics (AIMD) technique,⁵ we evaluated the thermodynamics of the defects formation and the diffusion kinetics of the conducting species in RRAM materials.^{6,7} The experimental and first-principles outputs were used to develop a stochastic model simulator, which we use to interpret the experimental set/reset dynamics, endurance and retention measurements.⁸ Modeling and simulations play an important role in understanding the atomistic mechanisms that take place during the manufacture, operation or storage of the resistive memory element. Through this talk we present our most recent advancements for oxide and Cu-based RRAM.

1. Z. Wei, et al., in *Electron Devices Meeting (IEDM)*, (2011), p. 31.4.1.

2. S. Shyh-Shyuan, et al., in Symposium on VLSI Circuits (2009), p. 82.

3. L. Seung Ryou, et al., 2012 IEEE Symposium on VLSI Technology, 71 (2012).

4. B. Govoreanu, et al., Ext. Abstr. SSDM Conf., Nagoya, Japan, pp.1005 (2011).

5. R. A. Miron and K. A. Fichthorn, Journal of Chemical Physics **119**, 6210 (2003).

6. S. Clima, et al., Applied Physics Letters **100**, 133102 (2012).

7. L. Goux, et al., in Symposium on VLSI Technology (VLSIT), (2012), p. 69.

8. R. Degraeve, et al., 2012 IEEE Symposium on VLSI Technology (2012).

10:40am **EM+PS-TuM9 Comparison of Surface Defects on Cleaved GaAs(110) and MBE Grown InGaAs(110)**, *M. Edmonds, T. Kent*, University of California San Diego, *R. Droopad*, Texas State University, *A.C. Kummel*, University of California San Diego

The dominant crystallographic face of InGaAs(001) based FinFETs is the (110)surface. These sidewall surfaces do not have metallic group III bonds and therefore with proper passivation might provide ideal interfaces to the gate oxide. It has been shown that with trimethyl aluminum (TMA) passivation of GaAs(110), monolayer nucleation density with zero lattice disruption can be achieved which is ideal for sub 0.5nm EOT scaling. Furthermore, dual passivation with an oxidant such as H₂O(g) has been shown to removes conduction band edge states associated with Al-Ga bonds results from TMA bonding. DFT studies confirm that TMA bridge bonds between the Ga and As atoms on the GaAs(110) surface while-OH from H₂O(g) dual passivation can readily insert into the Al-Ga bond thereby unpinning the surface. This study focuses on examining and characterizing surface defects and features of cleaved GaAs(110) in comparison with molecular beam epitaxy (MBE) grown InGaAs/InP(110) samples via scanning tunneling microscopy/spectroscopy (STM/STS) studies. Models of the various surface defects are proposed.

The MBE grown InGaAs/InP(110) samples are grown with an As₂ cap in order to protect the surface from oxidation. The samples are decapped at 350°C in an ultra-high vacuum chamber system prior to STM imaging. The initial STM image results show the surface contains a much higher step density compared to cleaved GaAs(110). The STM images of MBE grown InGaAs(110) also shows bright site features which have an average height of ~2.5Å and a site width variation from 1.8 nm to 3.6nm. These bright site features are consistent with excess As on the surface from an incomplete decapping procedure, or from surface undercoordinated atoms. A commercially available thermal gas cracker will be used to expose the surface to atomic hydrogen. It is believed this will remove any excess As on the surface and potentially passivating intrinsic surface defects. The dry in-situ atomic hydrogen cleaning of the MBE InGaAs(110) decapped samples will be compared with the cleaved GaAs(110) samples in aim to remove excess As₂ from the surface and make the InGaAs(110) surface comparable in low surface defect sites with cleaved GaAs(110).

11:00am **EM+PS-TuM10 Scalability of Doped Cubic HfO₂ Films**, *C. Adelmann, K. Opsomer*, Imec, Belgium, *S. Brizzi, M. Tallarida, D. Schmeisser*, BTU Cottbus, Germany, *T. Schram, S.A. Chew, N. Horiguchi, S. Van Elshocht, L.-A. Ragnarsson*, Imec, Belgium

HfO₂ has been the standard gate dielectric for MOSFETs for several technology nodes because of its large dielectric constant (~18 for amorphous or monoclinic HfO₂). To continue MOSFET scaling, replacement dielectrics for HfO₂ are of interest with an even larger dielectric constant. The polymorphism of HfO₂ offers the possibility to increase the dielectric constant by stabilizing the cubic phase of HfO₂ with a dielectric constant of ~30. The stabilization of the cubic phase has been demonstrated by introducing dopants (typically about 10%) such as Al, Si, or rare earths.

Numerous studies have demonstrated the advantage of doped cubic HfO₂ over undoped HfO₂ in terms of leakage vs. equivalent oxide thickness (EOT) for films with thicknesses of ~5-10 nm. These stacks lead to EOT values >>1 nm and are thus not relevant for future CMOS technology nodes. However, no clear advantage has been shown for scaled films with EOT values <1 nm.

In this paper, we study the behavior of Gd- and Al-doped HfO₂ in capacitors with EOT values below 1 nm (physical thicknesses of 2-3 nm). While Gd- and Al-doped HfO₂ show similar leakage for 10 nm thick films, capacitors with 2.5 nm Gd-doped HfO₂ show several orders of magnitude higher leakage than their Al-doped counterparts, indicating that the behavior for thick and thin films is not correlated. However, EOT vs. HfO₂ thickness measurements show that dielectric constants of the order of 30 can be maintained even for 2.5 nm thick films.

The ultimate scaling limits were explored for Al-doped HfO₂. It was found that the scaling of Al-doped HfO₂ is limited by the crystallization temperature of the films, which becomes too large for acceptable temperature budgets for (gate-last) MOSFET processing for thicknesses approaching 2 nm. This was confirmed by x-ray absorption spectroscopy at the O K-edge. Thinner doped HfO₂ films remain amorphous and exhibit a lower dielectric constant. In-situ XRD showed that the crystallization temperature of thick films (10 nm) was increased significantly by Al-doping. However, for 2 nm films, the comparison with undoped HfO₂ led to similar crystallization behavior indicating that the effects of thin films and doping do not necessarily add up. The lowest EOT values that could be achieved for gate-last MOSFET compatible processing were of the order of 8 Å including an interfacial SiO₂ contribution of about 4 Å. However, for such stacks, leakage current densities could be achieved which were about 2 orders of magnitude lower than HfO₂ capacitors with identical EOT values.

This indicates that doped HfO₂ films offer solutions for very low gate leakage at scaled EOT values down to values as low as 8 Å.

11:20am **EM+PS-TuM11 Advance of 3D-stackable Binary-oxide ReRAM for Storage-class Memory Applications**, *T.H. Hou, C.W. Hsu, I.T. Wang*, National Chiao Tung University, Taiwan, Republic of China
INVITED

Crossbar resistive-switching random access memory (RRAM) with a minimum cell size of 4F² has attracted much attention recently because of its superior memory performance, ultrahigh density, and ultimate scaling potential. The most anticipating emerging application of RRAM in future high-speed information systems is the storage-class memory (SCM) aiming to revolutionize inefficient data-storage hierarchy based on hard disks and present memory technologies. The requirements of the SCM technology include high data bandwidth, large storage capability, and low bit cost.

Replacing the current 2D memory with 3D memory architecture is one of the most feasible options to further increase storage capability per unit area. The types of 3D memory architectures can be divided into the 3D stacking of horizontal memory arrays and the bit-cost scalable (BiCS) 3D vertical memory. In the first part of this paper, two crossbar RRAM architectures, namely one diode-one resistor (1D1R) and one selector-one resistor (1S1R) fabricated using low process temperature applicable to the 3D stacking of horizontal memory arrays, are discussed. Their high-bandwidth parallel read/write capabilities are also investigated.

Despite the increase of bit density, the formation of multiple horizontal memory arrays requires a larger number of photolithography steps, and thus is unable to reduce bit cost. By contrast, multiple layers of thin film deposition and a small number of photolithography steps are used to produce high-density 3D vertical RRAM arrays potentially at extremely low cost. Stacking two individual selection and memory devices as a 1D1R or 1S1R cell is extremely challenging in 3D vertical RRAM arrays because the metal electrodes between two devices cannot be easily patterned at the vertical sidewall. Therefore, it is of great interest to develop a nonlinear RRAM device requiring no external selection device. In the second part of this paper, the latest advance of self-rectifying devices compatible to 3D vertical RRAM arrays are reviewed.

Manufacturing Science and Technology

Room: 202 B - Session MS+AS+BA+BI+PS+TF-TuM

IPF 2013-Manufacturing Challenges for Emerging Technologies: IV. Manufacturing Challenges: The Life Sciences

Moderator: D.G. Castner, University of Washington, L.J. Gamble, University of Washington

8:00am **MS+AS+BA+BI+PS+TF-TuM1 Microfluidics for Chemical Analysis**, *L. Carr, Q. Bai, R. Brennen, S. Post, G. Staples, K. Seaward, H. Yin, L. Martinez, D. Ritchey, K. Killeen*, Agilent Technologies **INVITED**

Chemical analysis is an essential tool for pharmaceuticals, environmental testing, food safety, forensics, energy and many other industries. The need for faster, more accurate and more sensitive measurements continuously pushes the limits of measurement technology and creates opportunities for advances in chemical analysis instruments and applications. One way in which this need can be addressed is by incorporating microfluidic devices in High Pressure Liquid Chromatography (HPLC). Pressure-based microfluidic chips have enabled a new class of reproducible integrated workflow devices that combine sample preparation, enrichment, and HPLC separation *with an integrated ESI/MS (Electrospray Ionization/Mass Spectrometry) interface* for high sensitivity nanoflow Liquid Chromatography-Mass Spectrometry (LC-MS). These devices have most commonly been fabricated using polymer, ceramic, and glass materials but the next generation of higher capacity and throughput microfluidic chips for LC-MS requires materials and structures capable of ultra high pressure operation. In this work, we describe the fabrication and performance of diffusion-bonded metal chips for high performance nano- and microflow LC-MS operation. The microfabrication technology required to make these devices includes semiconductor fabrication standards such as photolithography and thin film deposition, as well as laser ablation, electrochemical etching, and diffusion bonding. These novel metal devices exhibit state of the art performance in resolution and throughput for microfluidic LC-MS chips. These chips are an example of improvements in measurement sensitivity, resolution, speed, and ease of use that have been made possible by utilizing microfluidic devices for chemical analysis.

8:40am **MS+AS+BA+BI+PS+TF-TuM3 Challenges in the Fabrication of Nanoscale Devices for DNA Base Sensing**, *S. Papa Rao, J. Bai, E.A. Joseph, R.L. Bruce, M. Lofaro, M. Krishnan, M. Brink, M. Guillorn, S.M. Rossnagel, Q. Lin, J. Cotte, C. Jahnes, Smith, Gignac, Reuter, Nam, Astier, Wang, Stolovitsky, Goldblatt*, IBM Research Division, T.J. Watson Research Center **INVITED**

The fabrication of integrated circuits with increasingly fine geometries has required the development of advanced process technologies, which can be further refined for the purpose of building devices for biological applications. Applications such as sensing nucleotides in DNA require structures that are of the order of a few nanometers. This talk will focus on the specific challenges encountered in the fabrication of such nano-scale devices – broadly classified into materials-related challenges, unit-process challenges and process integration-related challenges. Issues such as dielectric integrity, metal recrystallization, and materials compatibility with chemistries used down-stream will be discussed. Dimension control during fabrication of ~10 nm sized structures was achieved through intense process development efforts of reactive ion etch and chemical mechanical planarization (both manufacturing-friendly techniques). Device layout issues that affect manufacturability will be presented. Finally, some of the important lessons learned in achieving a high yield of reliable devices through process-integration changes will also be discussed.

9:20am **MS+AS+BA+BI+PS+TF-TuM5 Nucleic Acid Synthesis and Applications**, *S. Laderman*, Agilent Technologies **INVITED**

The pursuit of perfect and practical *de novo* chemical syntheses of nucleic acids has been the foundation of a broad range of life science accomplishments over many decades in the past. Its further pursuit is enabling a broad range of opportunities many decades into the future. These themes will be elucidated by examining the precedents and improvements enabling high throughput genomics for research and diagnostics through the manufacturing of high quality DNA microarrays and complex pools of long oligonucleotides. Looking forward, new ways to synthesize RNA will enable deeper understanding and improved manipulations of cells, tissues and organisms. At the same time, multiple applications of synthetic biology are motivating additional focus on further advances in flexibly and cost-effectively constructing perfect DNA.

10:40am **MS+AS+BA+BI+PS+TF-TuM9 Single Molecule, Real-Time DNA Sequencing**, *S. Turner*, Pacific Biosciences **INVITED**

In this talk, I'll convey the story of the development and commercialization of Pacific Biosciences' Single Molecule, Real-Time DNA Sequencing technology. I will start with an overview of the method, how it works, and how it differs from sequencing methods that came before it. I will continue with a discussion of some key technology milestones, with an emphasis on the technological advances in materials engineering and nanofabrication. I'll finish by showing some examples of how this technology has transformed the field of DNA sequencing and genome analysis.

11:20am **MS+AS+BA+BI+PS+TF-TuM11 Opportunities and Challenges in the Biobased Products Manufacturing**, *J. Flatt, S. Bailey, S. Bower, D. Gibson, S. Farah, J. Butler, J. Hannon*, Synthetic Genomics **INVITED**

Biobased production of life's necessities, including food, fuels, chemicals and medicines provides a foundation for sustainable and geographically distributed manufacturing processes. Biobased manufacturing utilizes photosynthetic processes directly through conversion of carbon dioxide and light energy or indirectly through conversion of renewable biomass feedstocks to products. Biological cells (biocatalysts) are the operating systems for these biobased manufacturing processes. Rapid advances in synthetic biology enable the engineering of biocatalysts which can produce a broader range of products than previously possible, at high yields and productivities necessary for achievement of desired economics. Improvements in biocatalysts are achieved through modifications of DNA, which is the software of living systems. Significant advances in the costs, fidelity and speed of DNA synthesis, along with improving understanding of gene function and regulation is enabling the more rapid development of biocatalysts which achieve required performance for commercially viable manufacturing processes. The current state of the art of synthetic biology and technology trends which will impact future development of biobased processes will be discussed. Additional market-specific and process-specific challenges exist, and will be discussed in context of the specific examples taken from manufacture of synthetic vaccines, biobased chemicals and fuels. Recently, Novartis and Synthetic Genomics demonstrated the ability to successfully produce vaccines for prevention of seasonal influenza using synthetic DNA constructs, which significantly reduces the time from influenza strain identification to production of the vaccine seed. Development of this revolutionary process required significant improvement of the fidelity of DNA synthesis and assembly, which provides insight into the challenge of engineering more complex

biocatalysts. On the other end of the spectrum, phototrophic microalgae have great long-term potential to provide a sustainable and alternative source of food and liquid transportation fuels. Phototrophic microalgae can be cultivated using non-potable water on non-arable land. Techno-economic analysis (TEA) and life cycle assessment (LCA) both suggest that significant improvements in biocatalyst productivity and capital cost reduction will be required to achieve competitive economics. Maximum observed algal biomass productivities in the range of 20 to 25 g/m²/day are far lower than generally-agreed upon theoretically-achievable productivities based upon the actual solar energy available. Improvement of photosynthetic efficiency in mass culture is required for economical algal-based processes. Limited availability of light in mass culture also limits the maximum achievable cell density, which results in increased downstream processing costs. The challenges of "dilute solution economics" associated with commercial algae production and potential biological and engineering solutions will be discussed.

Plasma Science and Technology **Room: 102 B - Session PS1-TuM**

Plasma Sources

Moderator: S. Shannon, North Carolina State University

8:00am **PS1-TuM1 Non-ambipolar Electron Plasma and its Physical Properties**, *L. Chen, Z.Y. Chen, M. Funk*, Tokyo Electron America, Inc.

This report discloses a new type of plasma source: the Non-ambipolar Electron Plasma (NEP). Although, it is basically achieved by electron beam, its power coupling and plasma physical property differentiate itself from the generic e⁻-beam plasmas. Such differences open up potential applications that could have been difficult with the generic plasmas. The NEP system consists of two plasmas separated by a dielectric charged-species injector. Plasma-1 is the ground-referenced electron-source plasma (e.g., Ar) and it is an inductively coupled source (ICP) in this study for convenience reason. Plasma-2 is the NEP itself whose majority plasma-boundary is the DC-conductive accelerator with the remaining minority plasma-boundary being dielectric. NEP is typically molecular (e.g., N₂) in the pressure range of 1-3 mtorr and its accelerator voltage varied from $V_A=+80$ to $V_A=+600$ V. The NEP plasma potential (V_P) is boundary-driven. Therefore, NEP V_P tracks the accelerator voltage with its value just very slightly above V_A . The current across the dielectric charged-species injector is non-ambipolar: only electrons are transported from ICP to NEP and only positive-ions are transported from NEP to ICP. The non-ambipolar electron-current injected into NEP is in the range of 10s Acm⁻² with beam-energy $\sim eV_A$ and it heats NEP through beam-plasma instabilities. Its EEDf has a Maxwellian bulk followed by a broad energy-continuum connecting to the most energetic group with energies above the beam-energy. The remnant of the injected electron-beam power terminates at the NEP end-boundary floating-surface setting up sheath potentials from $V_S=80$ to $V_S=580$ V in response to the applied values of V_A . The floating-surface is bombarded by a space-charge neutral plasma-beam whose IEDf is near mono-energetic. When the injected electron-beam power is adequately damped by NEP, its end-boundary floating-surface V_S can be linearly controlled at almost 1:1 ratio by V_A . NEP does not have an electron-free sheath; its "sheath" is a wide presheath that consists of a thermal presheath followed by an "anisotropic" presheath, leading up to the end-boundary floating-surface. Its ion-current of the plasma-beam is much higher than what a conventional thermal presheath can supply. If the NEP parameters cannot damp the electron beam power sufficiently, V_S will collapse and becomes irresponsive to V_A .

8:20am **PS1-TuM2 Ion Energy-Angular Distributions in Dual Frequency Capacitively Coupled Plasmas Using Phase Control**, *Y. Zhang, M.J. Kushner*, University of Michigan

Dual frequency capacitively coupled plasmas (CCPs) provide the microelectronics fabrication industry with flexible control for high selectivity and uniformity. For a given low frequency (LF) bias, the magnitude and wavelength of the high frequency (HF) bias will affect the electron density, electron temperature, sheath thickness and so ion transit time through the sheath. These variations ultimately affect the ion energy and angular distributions (IEADs) to the substrate. For example, with higher HF power, the electron density and ion fluxes will increase, which will increase the etch rate. However, the higher HF power will also reduce the sheath thickness and reduce the ion transit time. This will produce more structure in the IEADs. One potential control mechanism for the IEADs is the relative phase of the LF and HF biases. In this paper, results from a two-dimensional computational investigation of Ar and Ar/C₄F₈/O₂ plasma properties in an industrial CCP reactor are discussed. The resulting IEADs are used as inputs to a feature profile model to assess etch profiles. In this

reactor, both the LF (2 MHz) and HF (up to 60 MHz) are applied to the lower electrode. The phase between the LF and HF is controlled.

To separately control rates of ionization and the shape of IEADs, the HF should be significantly higher than the LF. Under these conditions, there are many HF cycles per LF cycle. Although there are clear changes in the IEADs when varying the phase between the HF and LF, these changes are modulations to the IEADs whose shape is dominated by the LF. By sweeping the phase difference between the LF and HF, these modulations can be used to smooth and sculpt the IEADs. As the difference between the HF and LF becomes smaller, the IEADs become more sensitive to the phase differences between the HF and LF. These phase differences also affect the dc bias, an affect often call the electrical-asymmetry-effect when the frequencies are equal. Profile simulations are used to demonstrate possible control schemes for over-etch through phase control.

*Work supported by the Semiconductor Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

8:40am **PS1-TuM3 Investigation of Photo-Assisted Etching in Different Halogen-Containing Plasmas and Synergetic Effects of a Tandem Plasma System.** *W. Zhu**, *L. Liu*, *S. Sridhar*, *V.M. Donnelly*, *D.J. Economou*, University of Houston

Photo-assisted etching (PAE) of p-type Si in halogen-containing plasmas was discovered at sub-threshold ion energy in a Faraday-shielded, inductively coupled plasma (ICP). Halogen-containing feed gases (Br_2 , HBr , Br_2/Cl_2 and HBr/Cl_2) were explored and the strong dependence of PAE on different etchant gases was investigated. Sub-threshold etching rates in 50% halogen /50% Ar cw ICPs were ordered as 25% $\text{HBr}/25\% \text{Cl}_2 > 25\% \text{Br}_2/25\% \text{Cl}_2 > 50\% \text{Cl}_2 > 50\% \text{HBr} > 50\% \text{Br}_2$. H-atoms also caused isotropic etching in HBr plasmas; sub-threshold etching of patterned p-Si in other gases was anisotropic. PAE was much less important for Br_2 , with an etching rate 4 times slower than that for Cl_2 , under similar conditions. The dependence of PAE on incident photon energy was characterized by filtering incident photons with different wavelength to the sample surface. Vacuum UV was much more important than UV or visible light in inducing PAE. PAE is expected to cause substantial complications for processes that require low ion energies to achieve high selectivity and low damage, such as atomic layer etching. To address this issue, a tandem plasma system was developed to inject one plasma (upper plasma) into another plasma (lower plasma) separated by a grid. A "boundary electrode" (BE) in contact with the upper plasma could be biased to influence the plasma potential. The goal was to manipulate the electron energy distribution functions (EEDF), and possibly enhance ion-assisted etching compared to PAE. Plasma parameters and EEDFs were measured with a Langmuir probe over a wide range of power, pressure and position in cw Ar plasmas. With both plasmas powered (100 W lower plasma/ 500W upper plasma) at 10 mTorr, low energy electrons were depleted in the lower plasma when the BE was grounded. However, with 60 V bias on the BE, low energy electron depletion did not occur, and the high energy tail was enhanced. The reverse behavior was found in the upper plasma under the same conditions. Pulsed lower plasma with cw upper plasma injection was also explored. High plasma density of $2 \times 10^{11} \text{ cm}^{-3}$ with selectable, nearly-constant T_e (e.g. 0.8 eV) was achieved in the afterglow of the lower plasma at 10 mTorr.

9:00am **PS1-TuM4 Control of Energy Distributions in Inductively Coupled Plasmas using Tandem Power Sources.** *M.D. Logue*, University of Michigan, *W. Zhu*, *H. Shin*, *L. Liu*, *S. Sridhar*, *V.M. Donnelly*, *D.J. Economou*, University of Houston, *M.J. Kushner*, University of Michigan

In plasma materials processing, finer control of the electron energy distribution, $f(\epsilon)$, enables better selectivity of generating reactants produced by electron impact excitation and dissociation. This is particularly important in low pressure, inductively coupled plasmas (ICPs) where dissociation products often react with surfaces before interacting with other gas phase species. Under these conditions, fluxes to surfaces are more directly a function of electron impact rate coefficients than gas phase chemistry. Externally sustained discharges are able to control $f(\epsilon)$ by, for example, augmenting ionization independent of the $f(\epsilon)$ of the bulk plasma so that $f(\epsilon)$ can be better matched to lower threshold processes. In this case, the tail the $f(\epsilon)$ is lowered. Following the same logic, introducing additional losses by external means will produce an increase in the tail of $f(\epsilon)$. To achieve this control, a tandem (dual) ICP source has been developed. In this device, the primary (lower) source is coupled to the secondary (upper) source through a biasable grid to control the transfer of species between the two sources with the intent of controlling $f(\epsilon)$ in the primary source. A boundary electrode (BE) at the top of the system, along with the grid, can be dc biased to shift the plasma potential. This controls the energy of charged species passing into the primary source as well as ion energy distributions (IEDs) to surfaces.

* Coburn & Winters Student Award Finalist

Results will be discussed from a computational investigation of the control of and IEDs, in a tandem source ICP system at pressures of tens of mTorr. The model used in this study is the Hybrid Plasma Equipment Model (HPEM) with which $f(\epsilon)$ and IEDs as a function of position and time are obtained using a Monte Carlo simulation. $f(\epsilon)$ and IEDs will be discussed while varying the relative power in the primary and secondary sources, and dc biases (BE and grids) in continuous and pulsed formats. Results from the model will be compared to experimental data of $f(\epsilon)$ and IED obtained using a Langmuir probe and a gridded retarding field ion energy analyzer.

* Work supported by the DOE Office of Fusion Energy Science, Semiconductor Research Corp. and the National Science Foundation.

9:20am **PS1-TuM5 Si-Gate Etching in Radial Line Slot Antenna Plasmas: Control of Selectivity, Anisotropy and Loading.** *S. Voronin*, *A. Ranjan*, *H. Kintaka*, *K. Kumar*, *P. Biolsi*, TEL Technology Center, America, LLC

Shrinkage of transistors as dictated by Moore's law is required to make smaller, faster and less power-consuming devices at lower cost. 3-D gate transistors at 22nm technology node and beyond are needed to continue Moore's law. To obtain all these advantages of 3-D transistors, their fabrication has stringent requirements to the etch process such as high anisotropy, high selectivity to Fin and Gate mask films and minimum loading between isolated and nested lines. In addition, precise control over the gate profile from a vertical to a slightly negative angle is important for integration purposes. In this work we present highly selective 3D gate etching in halogen-based Radial Line Slot Antenna plasma. Having spatially separated plasma generation and plasma processing regions, RLSA™ etchers benefit of a very low electron temperature ($T_e \sim 1\text{eV}$) processing plasma discharge compared to conventional sources. Low electron temperature in the process plasma provides low dissociation rates of by-product and precursor gas, and ion bombardment of the structure at very low energies resulting in small iso-nested loading and very high process selectivity respectively. The ability of RLSA™ plasma sources to operate in a very wide range of the pressures allows the etch process well above 100mT. This leads to further decrease of the electron temperature in the bulk and the ion energy, providing notch-free etching of the structure. Changing by-product re-deposition rate by O_2 flow, etching times and bias power modulation regimes we can effectively control the gate profile from slightly tapered to slightly inverted tapered. Iso-nested delta can be minimized (and even reversed) by adjusting the process chemistry, bias power and pressure. Being very selective, RLSA™ plasma process allows very long over-etching times without damaging the mask. This makes the process universal, minimizes wafer-to-wafer profile variation and effective for etching the structures where Si layer thickness varies across the wafer. It is shown that artificial increase of the plasma electron temperature in the chamber to $\sim 2\text{eV}$ (an analog of a conventional plasma etcher) results in dramatic decrease of process selectivity to the oxide.

9:40am **PS1-TuM6 Vacuum-Ultraviolet Emission Spectra of Plasma-Processing Reactors.** *K. Mavrakakis*, *M. Nichols*, *W. Li*, *K. Katz*, University of Wisconsin-Madison, *J. McVittie*, *A. Hazeghi*, Stanford University, *S. Banna*, Applied Materials Inc., *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Plasma processing is an essential part of modern integrated circuit fabrication. The unique ability of plasmas to etch various materials in an anisotropic way and also to deposit thin films (PE-CVD) has made plasma processing the dominant method of processing modern IC circuits. One of the key problems with plasma exposure of low-k dielectric materials is that processing damage from vacuum ultraviolet emission (VUV) can take place. In order to further investigate the radiation-induced damage to dielectric films, it is important to determine whether different plasma reactors produce significant variations in their generated VUV spectra. In this work, we examine the VUV spectra generated by four unique plasma reactors using argon as the fill gas. They are: electron cyclotron resonance, capacitively coupled, neutral loop/ICP and microwave slot-plane antenna reactors. A McPherson Model 234 VUV monochromator was used for all measurements. The monochromator was fit to each reactor through a sequence of port aligners and collimation systems so that plasma light was well focused on the input slits. The output of the monochromator was focused on a sodium salicylate coating that scintillates in the visible portion of the spectrum and that light was detected by a photomultiplier. It was expected that the emission intensity varied with pressure and microwave power. However, depending on the reactor involved, this is not always the case. The resulting data shows that the emission intensity increases with the decrease of pressure and the increase of microwave power. The interesting result that we obtain is that argon does not always follow that trend over the same pressure and power ranges. As a result, it is important to optimize the processing conditions to minimize the VUV output whenever possible.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

10:40am **PS1-TuM9 Counteractions to Plasma Chamber Corrosions by Earthquake**, *T. Moriya*, Tokyo Electron, Japan **INVITED**

At the Japan's big earthquake in 2011, the plasma etching tools have received the big damages from the earthquake. Most of the etching tools were not able to be used normally. Many particles were contaminated to the wafers during etching process because the chambers were corroded by the outgassed acids during shutdown for several days. Just when the big earthquake attacked to the plant, some etching tools were on maintenance (doing wet cleaning). Because the technicians had to escape out of the clean room with leaving the tools as it is, some halogen gasses (fluorine, chlorine, bromine and so on) were outgassed from the process chambers. These gasses were combined with humidity in the room and became kinds of acids. In the process modules, the metal components were mostly corroded by the halogen-outgas related acids. Especially, as the gas feeding lines were contaminated, a lot of defects were created by the particles. In fact, a lot of particles were counted on wafers because of the corrosion related particle contaminations. By wet wiping of the process chambers, there were some good effects to the particle reduction but it was NOT completed. So, we checked and replaced many parts such as gas feeding line with using some special techniques. After that, the particle level was recovered to normal. The surface particle monitor was used to check the *in situ* particle level and worked effective. For checking the particles in the gas line, we suggest new method to observe the particles by using a wafer and creating a shockwave in the gas line. Since we already had the reference data which was obtained before the earthquake, we could compare between the normal condition and the current condition from the viewpoint of chamber contamination. There is another serious problem such as RF reflection alarms. This alarm means that the RF power cannot be supplied to the tool appropriately. As we changed some chamber parts, polished contacting areas and also changed the software parameters, and then, the RF reflection alarms were eliminated completely. The static chamber impedance measurement was also done to check the electric property. We also recorded the normal condition of the plasma chamber before the earthquake. So, we could compare between the normal condition and the current condition from the viewpoint of chamber electricity. If we want to manage the risks of corrosion by the earthquake, not only the surface particle count but also the static chamber impedance and the conditions of metal parts should be recorded periodically during the normal situation.

11:20am **PS1-TuM11 An Improved Cathodic Arc Plasma Source for Large Area Coatings**, *J. Kolbeck, A. Anders*, Lawrence Berkeley National Laboratory

Cathodic arc plasmas are widely used in the hard coatings industry to produce binary and ternary metal nitrides and oxynitrides, some of them exhibiting superhardness (> 40 GPa) and high oxidation resistance at elevated temperature. High deposition rates (10-100 nm/min) and self-ion-assistance to film growth are attractive features of the arc deposition process. However, microscopic droplets or "macroparticles" produced at cathode spots have prevented broader application of this technology, for example to optical coatings or to thin films used in the electronics industry. Here we report on the development of a linear cathodic arc plasma source that can be coupled to a linear macroparticle filter. We aim to develop a plasma source suitable for high-rate, large-area coatings, where films are essentially free of macroparticles. Operation and performance of the improved source will be demonstrated with metal and metal oxide films.

Specifically, we deposited aluminum-doped zinc oxide (AZO), a transparent conducting oxide which is non-toxic and made from abundant materials, a prime candidate for replacing the more expensive indium tin oxide (ITO) in some applications. AZO deposited on glass by filtered cathodic arc plasma exhibit very high electron mobility (some samples exceeding 50 cm²/Vs) for moderately high carrier concentrations (~ 10²⁰ cm⁻³), high transmittance in the visible and solar infrared (80-85%), with sheet resistance as low as 10 Ohms per square for relatively thick (~ 1 μm) films. AZO was also deposited on polycarbonate plastic at room temperature, with properties of interest to flexible electronics.

11:40am **PS1-TuM12 High Density Narrow Tube Ozonizer by Increased Barrier Discharge Frequency**, *J. Tsujino, T. Kitajima, T. Nakano*, National Defense Academy of Japan

Atmospheric plasmas are being general tool for various surface treatment applications, such as cleaning, sterilization, hydrophilic property control, etc. Among these applications, oxygen related radicals are the key species to influence the surface chemistry of the target. For the transport of the radical, spraying plasma processed gases to the object is commonly applied among these uses. There are certain reasons to develop high density

atmospheric plasma source which is compact and able to be introduced or "retrofit" to the current chemical processing systems. In the current study, we are developing the high frequency atmospheric ozonizer plasma source in general 1/4 inch O.D. tube which gives high density ozone.

High frequency barrier discharge at 280 kHz consists of the alumina tube, the copper grounded electrode, and the aluminum drive electrode. (shown in fig. 1) The aim of MF range of frequency is to shift power deposition target to electrons from ions, and to increase the barrier discharge frequency. High voltage for the barrier discharge (0.5 mm gap) is produced by the LC resonance circuit (fig. 2).

Comparison of ozone density between 50 Hz (0.8 g /Nm³, 40 kVpp) and 280 kHz (30 g/Nm³, 6.5 kVpp) shows the production rate is increased 40 times for realistic voltage range (fig. 3).

V-I characteristic of 280 kHz (fig. 4) shows the discharge current and power is increased steeply around 6 kVpp that corresponds to the rapid increase of ozone production rate.

The increase of power with voltage is explained by the change of waveform (fig. 5). Small change of the voltage leads to the forwarding of the current phase and increase of barrier discharge frequency.

The power efficiency of the ozonizer is 19 g /kWh which is comparable to the commercial small scale unit.

Plasma Science and Technology
Room: 104 C - Session PS2-TuM

Advanced FEOL/Gate Etching

Moderator: G.Y. Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS2-TuM1 Evaluation of Highly Selective ZrO₂ and HfO₂ based Hard Mask Stacks for sub 30 nm Node Dry Etch Pattern Transfer**, *J. Paul, X. Thrun, S. Riedel, M. Rudolph*, Fraunhofer Institute for Photonic Microsystems (IPMS-CNT), Germany, *S. Wege*, Plasway, Germany, *C. Hohle*, Fraunhofer Institute for Photonic Microsystems (IPMS-CNT), Germany

The main challenge for future leading edge patterning results from an aggressive trend in reduction of resist thickness for high resolution lithography. For instance, at the 25 nm DRAM technology node, a maximum resist thickness of 30 to 60 nm is predicted by the ITRS for 2014. Moreover, the hard mask thickness will be limited by the thickness of the photoresist. Different approaches such as multi-layer resists were discussed to enable pattern transfer with reduced resist thicknesses. These approaches are focusing more and more on innovative underlayer materials and anti-reflective coatings providing a higher etch selectivity. Novel hard mask concepts with reduced layer thickness and improved etch selectivity can be seen as an alternative strategy.

The present work reveals a new hard mask concept based on ZrO₂ and HfO₂ materials in combination with a SiO₂ capping layer to provide the high resolution pattern transfer into the substrate. An excellent silicon and carbon etch selectivity is focused for semiconductor manufacturing. Besides the scaling capability, the hard mask concept was evaluated in terms of etch selectivity, hard mask roughness, removal of remaining hard mask after etch and cost-saving deposition method. Therefore atomic layer and spin-on depositions of HfO₂ and ZrO₂-based hard masks were investigated. Additionally the influence of dopants on the etch properties and patterning results was evaluated.

The dual hard mask concept was demonstrated using 35 nm thin layers of ZrO₂ and HfO₂ based material and 45 nm SiO₂ deposited on 300 nm wafers. The resist (50 nm) was directly applied on the hard mask and arrays of holes and trenches (CD 30 nm to 500 nm) were printed by electron beam direct writing. The hard mask open was performed in a two-step process by CCP and ICP type etch chambers. The hole and trench pattern were transferred into silicon and carbon by dual-frequency MERIE CCP and triple-frequency CCP type etch system, respectively. Finally the remaining mask was removed by wet etching without deterioration of the etched profiles. This sequence allowed the preparation of structures with aspect ratios up to 20:1 (CD 30 to 60 nm) and revealed a high overall hard mask selectivity to silicon e.g. ~ 35:1.

This new dual-layer concept enables a significant reduction of overall hard mask thickness and the patterning of 30 nm structures and a potential technology approach for more critical structures in the sub 20 nm range.

8:20am **PS2-TuM2 Approach to LER/LWR Improvement with Combination of DCS Technology and Newly Developed Resist Material.** *M. Honda, K. Kobayashi,* Tokyo Electron Miyagi Limited, Japan, *M. Yamato, K. Oyama, H. Yaegashi, H. Mochiki,* Tokyo Electron Limited, Japan

Due to the continued scaling in semiconductor industry, reducing line edge roughness (LER) and line width roughness (LWR) during photoresist mask pattern transfer by etch becomes increasingly important at 10nm and beyond.

Our previous studies showed that successful LER/LWR reduction was achieved by optimizing plasma treatment conditions and DC superposition (DCS) technology which is resist hardening by highly energetic electrons incident onto wafer in DC+RF hybrid capacitively-coupled reactor [1,2]. On the other hand, newly developed PMMA-based 193nm resist material with low etching durability has been proposed for the further reduction of LER/LWR [3,4].

In this paper, we investigated the effect and mechanism of DCS technology on newly developed 193nm resist material. As a result, we achieved LER=1.2nm with new 193nm resist material by etching durability enhancement of DCS technology. We also found that DCS technology is very effective for CD shrink control especially required for future BEOL patterning. This integrated solution of resist material modification and DCS technology will allow us for expanded process window for LER/LWR control at 10nm and beyond critical patterning etch.

Reference

- [1] M. Honda et al., Proc. of SPIE 8328-09 (2012)
- [2] M. Honda et al., AVS 59th Int. Symp. & Exhibit. (2012)
- [3] H. Yaegashi et al., Proc. of SPIE 8325-11 (2012)
- [4] K. Ohmori et al., Proc. of SPIE 8325-12 (2012)

8:40am **PS2-TuM3 Metrology and Linewidth Roughness Issues during Complex High-k/Metal Gate Stack Patterning for sub-20nm Technological Nodes.** *E. Pargon, M. Fouchier,* CNRS-LTM, France, *O. Ros Bengoechea,* STMicroelectronics, *J. Jussot,* UJF, France, *E. Dupuy, M. Brihoum,* CNRS-LTM, France **INVITED**

Gate Line Width Roughness (LWR) or Line Edge Roughness (LER) is considered today as a factor limiting CMOS downscaling. No technological solution is currently known to reach the 1.7nm gate LWR required for the sub-20nm technological node. The origin of the LWR/LER of the final transistor gate is mainly attributed to the significant roughness of the photoresist (PR) pattern printed by the lithography step, which is partially transferred into the gate stack during the subsequent plasma etching steps. Thus, those passed few years, many efforts have been focused on the development of post-lithography resist treatments in order to minimize the LWR of resist patterns prior to plasma transfer. Another issue related to LWR/LER is the availability of accurate and convenient metrology tools for their evaluation. The status on LER/LWR metrology is that there is today no reliable and efficient metrology equipment to determine LWR at the very bottom of structures, where the key LWR information lies, as well as to estimate sidewall roughness of complex high-k/metal gate stacks composed of a multitude of very thin layers of dielectrics, metals and semiconductors.

We first propose a method based on AFM to measure LER accurately down to feature bottom for any types of pattern profiles (anisotropic, tapered or re-entrant). We will show that it presents a great potential for better understanding the mechanism of LER transfer during complex high-k/metal gate stack patterning.

Various post-lithography processes based on thermal or plasma treatments are also evaluated to decrease resist pattern LWR. A particular attention is paid to characterize the roughness by its frequency spectrum since for gate applications low frequency roughness components remain the key issue. We will show that optimized plasma treatment for LWR reduction may use plasma conditions leading to intense optical emission in the vacuum ultra violet (VUV) range (<200nm), and limiting the deposition of carbon outgassed resist byproducts on the pattern sidewalls. Moreover, we show that thermal process applied after plasma treatment can improve further the resist LWR, provided that no carbon deposition be previously formed on the resist sidewalls during the plasma treatment. The best available post-lithography treatment allows a 50% LWR reduction, while maintaining the critical dimension control. Finally, the developed AFM technique is used in comparison with CD-SEM to study the transfer of the reduced resist LWR resist into the gate stack during the patterning.

9:20am **PS2-TuM5 Possible Si Damage Formation and Redeposition in Vertical Gate Etching Processes by HBr Plasmas.** *Y. Muraki, H. Li, T. Ito, K. Karahashi,* Osaka University, Japan, *M. Matsukuma,* Tokyo Electron Ltd., Japan, *S. Hamaguchi,* Osaka University, Japan

Reactive ion etching (RIE) by halogen-based plasmas such as HBr plasmas are widely used for Si etching in semiconductor manufacturing processes. It has been known that, for a Si surface, Br ions have high etching yields, high selectivity over SiO₂ and SiN, and high etching anisotropy. However, in recent years, as non-classical CMOS structures such as vertical multi gates have been introduced for near-future devices, there has been a concern on possible damages caused by highly energetic hydrogen ions (H⁺) that hit a Si surface even at grazing angles. For vertical multi gates, the Si surfaces subject to direct ion bombardment function as gate channels, ion bombardment damage to the surface must be minimized. In this study, we have evaluated sputtering yields of Si by Br⁺, H⁺ and SiBr⁺, as functions of incident energy in the range from 300 eV to 1000eV as well as functions of the incident angle. We have also examined Si substrate damages caused by ion bombardment by transmission electron microscopy (TEM) and High-resolution Rutherford Backscattering Spectrometry (HRBS). It has been found that there is strong angle dependence of the Si etching yield by Br⁺ ion irradiation, which indicates that Br⁺ ion etching has also an aspect of physical sputtering despite its high chemical reactivity with Si. Although, in actual HBr plasma processing, simultaneous surface passivation by Br radicals makes its Si etching more chemical, the nature of physical sputtering by energetic Br⁺ ion bombardment ensures anisotropic etching. The depth of damages in a Si substrate caused by Br⁺ ion bombardment, on the other hand, decreases with its angle of incidence as Br⁺ ions cannot penetrate deeply into the substrate at higher incident angles. However, it has been also found that energetic H⁺ ions can be damaging to the Si surface even at large incident angles since, due to their small mass, incident H⁺ ions are scattered nearly isotropically when they hit the substrate surface. In addition, due to their small atomic size, H⁺ ions penetrate far more deeply than Br⁺ ions do. Furthermore it has been found that SiBr_x⁺ ions can be deposited at low energy. Since, at relatively high-pressure, SiBr_x⁺ ions can be rather abundant in HBr plasmas for Si etching. Therefore care must be taken in developing HBr etching processes for vertical multi gates to avoid surface damages by H⁺ ions and to control the profiles despite incident and/or re-sputtered species with higher sticking probabilities.

9:40am **PS2-TuM6 Impact of Etch Processes Over Dimensional Control and LWR for 14nm FDSOI Transistor Gate Patterning.** *O. Ros,* ST Microelectronics, France

Microelectronic evolution still relies on higher transistor gate integration and transistor size reduction. The major issue related to transistor downscaling is the control at the nanometer range of two main variability sources: Critical Dimension uniformity (CDU) and the Line Width Roughness (LWR). Nowadays, the best lithography conditions allow the definition of photo-resist patterns with a minimum roughness of 4-5nm and a CDU at 3 σ < 2.5nm (for 28nm technologies), which will be then transferred into the underlying layers by etch processes. To improve lithography performances, post-lithography treatments such as plasma treatments have so far been introduced to increase photo-resist stability and to improve LWR and CDU during pattern transfer. If such a strategy allows to meet the CDU and LWR requirements of the 32 nm technological node, we will show that the unique use of conventional post-lithography treatments is not anymore efficient to address the specifications of the latest CMOS and beyond CMOS technologies. They indeed introduce several pattern deformations such as resist flowing and gate shifting, that inevitably cause process variability. Thus, new patterning strategies have to be implemented to ensure CMOS downscaling.

In this study, we compare different etch chemistry combinations in order to define the best etch process condition to pattern a 14 nm Fully Depleted Silicon On Insulator (FDSOI) gate stack guaranteeing control over the main variability sources, CD uniformity and LWR. We show that a combination of photo-resist pre-treatments and an optimization of each material's etch process are required to ensure process control during typical FDSOI gate stack patterning (consisting in Photoresist/Silicium Anti Reflective Coating (SiARC)/Carbon layer (SoC)/Oxide Hard Mask (HM)/Polysilicium/High-K Metal Gate (HKMG)). As an example, promising results over SiARC opening step show that the introduction of a new etch chemistry followed by an optimized trim step leads to better defined patterns and a 25% improvement over LWR compared to the values obtained after standard SiARC opening.

10:40am **PS2-TuM9 FinFET Patterning: Promises and Challenges of SIT² for Fin Formation for sub-40 nm Pitch Features**, *S. Mignot*, GLOBALFOUNDRIES U.S. Inc., *I.C. Estrada-Raygoza*, *H. He*, IBM, *K. Akarvardar*, *J. Cantone*, GLOBALFOUNDRIES U.S. Inc., *B. Doris*, IBM, *A. Jacob*, GLOBALFOUNDRIES U.S. Inc., *S. Schmitz*, *J. Lee*, *P. Friddle*, *M. Goss*, Lam Research Corp

FinFET device enables scaling of CMOS technology due to its reduced short-channel effects. Realization of this potential is highly dependent on achieving ideal fin structure shape and reducing variability at the front-end of the process. In particular, fin width and high uniformity are critical. The width of the fin structure is typically required to be at a critical dimension that is below resolution limit of single exposure conventional 193nm immersion lithography (i.e., <40nm half pitch). Over the last couple of technology nodes one common technique for fin formation at tight pitch is to use patterning process flow of Sidewall Image Transfer (SIT).

In this publication, a Double Sidewall Image Transfer (SIT²) etch patterning process has been demonstrated for sub 40nm pitch at fin step. The SIT² process scheme that has been explored includes silicon mandrel etch followed by Nitride Spacer deposition and etch. Process integration at this level requires a process free of collapsing features and with minimum pitch variations. SIT² main etch challenges will be reviewed. Etch process mechanisms both physical and chemical have been investigated to achieve silicon etch fin pattern and selectivity to the hard mask and spacer materials as well as uniformity for both macro-to-macro and across wafer.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:20am **PS2-TuM11 Stack Patterning Challenges for the FinFET Architecture**, *A. Banik*, *S. Kanakasabapathy*, *S. Burns*, *A. Aiyar*, *M.J. Brodsky*, IBM Corporation

The FinFET device architecture, presents certain new gate patterning challenges. The gate stack aspect ratio is higher, compared to previous planar generations. We will illustrate how this aspect ratio is due to the presence of fins and the need for higher overetch in the offset spacer patterning. Controlling the gate profile to be vertical in both isolated and dense lines is challenging as the gate height increases. Further, Double expose Double etch (DE²) has been the process of record since the 45nm node. This is driven by the need for better tip-to-tip control while maintaining across chip line width control (ACLV). It has typically relied on pattern assembly through DE², in the gate hardmask layers, followed by a transfer etch into the underlying gate polysilicon. In such a scheme, the dense-iso gate critical dimension (CD) variation is exacerbated by the tall gates needed for the FinFET architecture. Legacy techniques, such as higher ion energy in the polysilicon etch, are limited by the large overetch needed past the fin tops, and selectivity needed in that step.

We present in this paper, patterning sequencing options that reduce the dense-iso challenges for the unique FinFET geometry. We will present data that shows how Lithography and etch process modifications are needed to enable such modified patterning sequences.

This work has been performed by the independent SOI technology development projects at the IBM Microelectronics Division Semiconductor Research & Development Center, Hopewell Junction, NY 12533

11:40am **PS2-TuM12 Mechanisms of Etching and Selectivity for FINFET Gate Low-k Spacer using RLSATM Microwave Plasma Reactor with Radial Line Slot Antenna**, *A. Raley*, *B. Parkinson*, *A. Ranjan*, *S. Keisuke*, *K. Kumar*, *P. Biolsi*, TEL Technology Center, America, LLC

Spacer design and materials for planar and FINFET transistors has become increasingly critical as gate length is shrinking. For technology node of 22nm and beyond, fringe capacitance between gate and contact/epi-facet are becoming significant component of device degradation.¹ Spacer films with low dielectric constant (Low-k spacer) minimize parasitic capacitances because low permittivity can reduce gate-fringing field effects. Several materials and methods for low-k spacers have been reported showing improved device performance^{2,3}. Incorporation of oxygen, boron, and carbon into SiN spacer film to form SiOCN or SiBCN low-k films with oxygen, boron and carbon contents tuned to minimize k value and provide good leakage performance are two of the low-k avenues being explored. Etching of these materials versus conventional SiN spacer has been characterized in simulated wafer product environment and demonstrated on FINFET structure using RLSATM microwave plasma reactor with radial line slot antenna. RLSATM microwave plasma source yields high ion flux with tunable ion energies to control polymer passivation. This is key to achieve the high SiN/Si and SiN/SiO₂ selectivities mandated by long over etch requirement in the FINFET spacer scheme. The etching mechanisms of low-k films have been compared to that of SiN and SiO₂ and it has been shown to strongly depend on the oxygen content of the film. A systematic study on process parameters impact on low-k film etching rate versus SiN

and SiO₂ will be presented. Optical emission spectra analysis of relative intensities of the following species F, B, H, CF₂, and O will be analyzed. Impact of electron energy distribution (tuned by source power and pressure) and ion angular energy distribution (tuned by bias power and pressure) on the species considered will be shown to explain selectivity mechanisms and etch rate trends.

1. Kuhn, K, "22 nm Device Architecture and Performance Elements", IEDM, 2008
2. Ko, C.H, "A novel CVD-SiBCN Low-k spacer technology for high-speed applications", VLSI Technology Symposium, 2008, p108-109
3. Huang, E., "Low-k spacers for advanced low power CMOS devices with reduced parasitic capacitances", SOI Conference, 2008. SOI. IEEE International, p10-20

Tuesday Afternoon, October 29, 2013

Energy Frontiers Focus Topic

Room: 101 A - Session EN+AS+PS-TuA

Water Splitting and Carbon Dioxide Conversion

Moderator: D. Lutterman, Oak Ridge National Laboratory

2:00pm EN+AS+PS-TuA1 Turning CO₂ into Liquid Fuel, *M. Kanan*, Stanford University **INVITED**

The longstanding reliance on fossil fuels as the principal energy source for society has boosted the atmospheric CO₂ concentration to a level that is unprecedented in modern geological history. Since the use of carbon-containing fuels is entrenched in society, controlling the atmospheric CO₂ concentration may ultimately require recycling CO₂ into liquid fuels and commodity chemicals using renewable energy inputs. Arguably the greatest challenge for this vision is to develop efficient CO₂ reduction catalysts. This talk will describe our development of "oxide-derived" metal nanoparticles as electroreduction catalysts. Oxide-derived metal nanoparticles are prepared by electrochemically reducing metal oxide precursors. This procedure results in highly strained metal nanocrystals, as determined by grazing incidence synchrotron x-ray diffraction. I will describe examples of these catalysts that electrochemically reduce CO₂ to CO with exceptional energetic efficiency as well as a catalyst that selectively reduces CO to two-carbon oxygenates. The catalysts operate in water at ambient temperature and pressure and are remarkably robust. The reduction mechanisms will be discussed based on electrokinetic measurements. Metal oxide reduction represents a "top-down" approach to metal nanoparticle synthesis that can result in unique surface structures for catalysis.

2:40pm EN+AS+PS-TuA3 Efficient Conversion of CO₂ to Fuels using Inexpensive Cathode Materials, *J. Rosenthal, J. DiMeglio, J. Medina-Ramos*, University of Delaware

The wide-scale implementation of solar and other renewable sources of electricity requires improved means for energy storage. An intriguing strategy in this regard is the reduction of CO₂ to CO, which generates an energy rich commodity chemical that can be coupled to liquid fuel production using Fischer-Tropsch methods. To this end, we have developed an inexpensive Bismuth Carbon Monoxide Evolving Catalyst (Bi-CMEC) that can be formed upon cathodic polarization of an inexpensive carbon or metallic electrode in acidic solutions containing Bi³⁺ ions. This catalyst can be used in conjunction with ionic liquids and other weak organic acids to effect the electrocatalytic conversion of CO₂ to CO with appreciable current density at low overpotential. The systems to be described are selective for production of CO, operating with very high Faradaic efficiency for conversion of CO₂ to this valuable product. As such the ability of this electrocatalyst system to drive production of CO from carbon dioxide is on par with that which has historically only been observed using expensive silver and gold cathodes.

4:00pm EN+AS+PS-TuA7 Power Curves of the Artificial Leaf, *D. Nocera*, Massachusetts Institute of Technology **INVITED**

An artificial leaf can perform direct solar-to-fuels conversion via water splitting. The artificial leaf is a buried junction, in which the rectifying junctions are protected from solution or "buried". Whereas water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation in a solution junction PEC device, in a buried junction device, catalysis is separated from the current rectification, charge separation, and photovoltage generation, which occur at the internal junction. The buried junction photoelectrochemical (BJ-PEC) cell is free from many of the design limitations of a traditional solution junction photoelectrochemical (SJ-PEC) cell. First and foremost, in a SJ-PEC, water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation. Accordingly, most candidate materials are based on metal-oxides. Decades of research have shown that it is extremely difficult to produce a competent photovoltaic (PV) material that at the same time is capable of facilitating the demanding four-electron, four-proton chemistry of water splitting. Second, in a SJ-PEC, the band edges of the flatband potentials of the semiconductor must straddle the thermodynamic potentials of OER and HER under the conditions of operation. These foregoing limitations are circumvented in a buried junction device. In a BJ-PEC, water-splitting catalysis is separated from the internal junction where current rectification, charge separation, and photovoltage generation occur. Accordingly, the OER and HER catalysts may be optimized independently from the PV device such that the maximum power characteristics of the PV and catalyst may be matched independently. Of equal significance, in a BJ-PEC, the potential drop across the outer Helmholtz layer will adjust

automatically to move the Fermi levels to energetic positions that allow the water splitting reaction to proceed. For this reason, the photovoltages produced at buried junctions need not be fixed relative to a specific material flatband potential and consequently there is no requirement for the flatband potentials of the semiconductors to straddle the thermodynamic potentials of the OER and HER. There simply has to be sufficient potential generated by the PV device to enable water splitting. This talk will focus on the analysis of Tafel and photovoltaic power curves. The presented analysis highlights the importance of matching the electrochemical load of the water splitting catalyst to the onset of maximum current of the PV component, drawing a clear link between the kinetic profile of the water splitting catalyst and the SFE of devices such as the artificial leaf.

4:40pm EN+AS+PS-TuA9 Transient Plasma for Green Technologies: Reduced Emissions, Greenhouse Gas Reduction, and Improved Combustion Efficiencies, *M. Gundersen*, University of Southern California **INVITED**

Transient plasma, that is, plasma during a formative, short time period prior to equilibration of a plasma electron energy distribution, is studied for applications to the fundamental improvement of fuel-burning engine efficiency in fuel-air mixtures, and in exhaust streams. This transient plasma requires operation with short (<100ns) pulsed high voltage, and typically requires only small pulse energy (10mJ to <1J). Transient plasma has been demonstrated shows promise for improving engine efficiency through improved combustion efficiency, and has been demonstrated to be efficient for NO_x conversion. Results for studies of engine types including internal combustion engines, pulse detonation engines, will be discussed, and ideas for future directions will be presented. This work has been supported by the AFOSR, ARO, and the TCC Corp.

5:20pm EN+AS+PS-TuA11 Activation of CO₂ using Non-equilibrium Plasma: Mechanisms and Power Efficiency, *M.C.M. van de Sanden, A.P.H. Goede, M. Graswinkel, W. Bongers*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands, *F. Brehmer, S. Welzel, R. Engeln*, Eindhoven University of Technology, Netherlands **INVITED**

Sustainable energy generation by means of, either photovoltaic conversion, concentrated solar power or wind, will certainly form a significant part of the energy mix in 2025. The intermittency as well as the temporal variation and the regional spread of this energy source, however, requires a means to store and transport energy on a large scale. In this presentation the means of storage will be addressed of sustainable energy transformed into fuels and the prominent role plasma science and technology can play in this great challenge.

The storage of sustainable energy in these so called solar fuels, e.g. hydrocarbons and alcohols, by means of *artificial photosynthesis* from the feedstock CO₂ and H₂O, will enable a CO₂ neutral power generation infrastructure, which is close to the present infrastructure based on fossil fuels. The challenge will be to achieve *power efficient* dissociation of CO₂ or H₂O or both, after which traditional chemical conversion (Fischer-Tropsch, Sabatier, etc.) towards fuels can take place.

Most of the research efforts are directed at the splitting of water in hydrogen and oxygen. However, no efficient catalytic or traditional chemical alternative is yet available. A promising route is the dissociation or activation of CO₂ by means of plasma, possible combined with catalysis. Taking advantage of non-equilibrium plasma conditions to reach optimal energy efficiency the FOM institute DIFFER has started its solar fuels program at the beginning of 2012 focusing on CO₂ plasma dissociation into CO and O₂. The plasma is generated in a low loss microwave cavity with microwave powers up to 10 kW using a supersonic expansion to quench the plasma and prevent vibrational-translational relaxation losses. New ideas on the design of the facility and results on power efficient conversion (more than 50%) of large CO₂ flows (up to 75 standard liter per minute with 11% conversion) as determined from calibrated mass spectrometry measurements at low gas temperatures will be presented.

Manufacturing Challenges of Nanoscale Patterning**Moderator:** E.B. Svedberg, The National Academies**2:00pm MS+AS+EL+EM+PS+TF-TuA1 Alphabet-Based Template Design Rules - A Key Enabler for a Manufacturable DSA Technology, H. Yi, H.-S.P. Wong, Stanford University INVITED**

Block copolymer DSA is a result of spontaneous microphase separation of block copolymer films, forming periodic microdomains including cylinders, spheres, and lamellae. Among all the various self-assembled structures, cylinder patterns have attracted specific interest due to their great potential in patterning electrical contacts in Integrated Circuits (ICs). Due to the random distribution of electrical contacts in layouts as well as the continuous scaling of IC circuits, patterning contacts has become increasingly challenging for traditional optical lithography. Due to the advantage of low cost and sub-20 nm feature sizes, block copolymer directed self-assembly (DSA) is a promising candidate for next generation device fabrication.

Traditionally, the study of DSA has been focused on achieving long range order and a periodic pattern in large area. Chemoepitaxy approaches including using chemical patterns of preferential affinity on the substrate surface or controlling pattern formations by tuning annealing conditions have been investigated and developed. They can improve the long range order self-assembly quality and lower the defect density over large areas. In order to use DSA to pattern the randomly distributed contacts in IC layouts, we adopt physical (topographical) templates to form irregularly distributed cylindrical patterns. Topographical templates use strong physical confinements in lateral directions to alter the natural symmetry of block copolymer and guide the formation of DSA patterns. Previously we have demonstrated that for the first time the self-assembled features can be almost arbitrarily placed as required by circuit fabrication and not limited to regular patterns, by combining templates of different types on one wafer. These various templates are akin to the letters of an alphabet and these letters can be composed to form the desired contact hole patterns for circuit layouts. The capability of arbitrary placement is demonstrated in industry-relevant circuits such as static-random-access-memory (SRAM) cells and standard logic gate libraries at a dimension that is the state-of-the-art semiconductor technology today [1]. To enable introduction of DSA into manufacturing we developed a general template design strategy that relates the DSA material properties to the target technology node requirements. This design strategy is experimentally demonstrated for DSA contact hole patterning for half adders at the 14 nm and 10 nm nodes [2].

Reference:

[1] H. Yi et al. *Adv. Mater.*, 2012.[2] H. Yi et al. *SPIE*, 2013.**2:40pm MS+AS+EL+EM+PS+TF-TuA3 Characterizing the Sensitivity of Block Copolymer Directed Self-Assembly Processes to Material and Process Variations, C. Henderson, A. Peters, R. Lawson, P. Ludovice, Georgia Institute of Technology**

Future scaling of integrated circuits (IC) is in jeopardy due to a number of challenges related to both future material and process requirements that are needed to allow for fabrication of sub-20 nm IC devices. One of the most critical challenges is that of developing patterning technologies that can allow for formation of sub-20 nm patterned structures in a fast and economically viable manner. Due to difficulties with alternative technologies, techniques that can extend the use of current 193 nm optical lithography in a cost effective manner would be very attractive. Directed Self-Assembly (DSA) using block copolymers to perform pitch subdivision of lithographically generated primary patterns is one such promising technology. In this technique, a lithographic method is first used to define a topographic or chemical template pattern on a surface. This surface is then coated with a block copolymer that is further processed to induce microphase separation. The presence of the topographic or chemical patterns on the surface aligns, registers, and provides long range order to the formed block copolymer patterns. This microphase separation-based patterning process utilizes the propensity of the block copolymer to naturally form nanometer scale patterns whose size are dictated by the polymer block molecular weight.

The overarching goal of our work has been to develop both new block copolymers that can enable sub-20nm DSA patterning and to develop the experimental and modeling tools needed to understand the limits of such processes. In this paper, we will review our recent systematic studies of block copolymer DSA processes using state-of-the-art molecular dynamics simulations. The aim of these studies has been to identify the important

material and process factors that affect the DSA process and to quantify the sensitivity of the DSA process to these factors. For example, the influence of polymer block molecular weight control and polydispersity on patterning have been rigorously quantified. Furthermore, processing factors such as guiding pattern mis-sizing and low level surface topography in the guiding pattern and their effect on DSA patterning have been studied in detail. Studies have also been performed via simulation using thermodynamic integration methods to calculate the free energy of defects in such DSA systems and the sensitivity of such defect free energies to important material and process parameters. We will review the outcomes of these studies to illustrate what the important material and process challenges will be in adapting block copolymer DSA methods into a manufacturable technology.

3:00pm MS+AS+EL+EM+PS+TF-TuA4 DSA Patterning for sub-40 nm Pitch Features, I.C. Estrada-Raygoza, C. Liu, Y. Yin, J. Abdallah, IBM Albany Nanotech Center, S. Mignot, GLOBALFOUNDRIES U.S. Inc., B.G. Morris, M.E. Colburn, IBM Albany Nanotech Center, V. Rastogi, N. Mohanti, A. Raley, A. Ko, TEL Technology Center, America, LLC

As the semiconductor industry targets sub-40 nm pitch features, there will be a necessity for new patterning techniques which allow for the extension beyond single ArF-immersion patterning capability of 38 half pitch features. To meet today's aggressive design requirements, double patterning techniques, such as Pitch Splitting (PS) Lithography and Sidewall Image Transfer (SIT), have been widely used. Below 38 nm pitch design the industry has looked toward Extreme Ultraviolet (EUV), Double Sidewall Image Transfer (SIT2) and Directed Self-Assembly (DSA) as strong emerging candidates. A major component to the success of the DSA technique is the development of effective etch processes. This talk targets to discuss the challenges and innovations of the plasma etch process on sub-40 nm pitch features produced by DSA chemo and grapho-epitaxy guiding patterns. Each DSA scheme presents different challenges, depending of the aspect ratio, density of the patterns and etch stack materials, but in general, the parameters that have been studied are selectivity to both masking and etched materials, across wafer profile uniformity, critical dimension (CD) uniformity and line-edge/line-width roughness (LER/LWR). This work was performed by the Research Alliance Teams at Albany IBM Research and Development Facilities.

4:40pm MS+AS+EL+EM+PS+TF-TuA9 Advanced Gate Patterning Techniques for 14nm Node and Beyond, F.L. Lie, R. Jung, Y. Yin, A. Banik, S. Kanakasabapathy, J.C. Arnold, S. Seo, B. Haran, IBM Corporation, Y. Moon, L. Jang, S. Bentley, GLOBALFOUNDRIES U.S. Inc., H. Kang, D. Bae, Samsung Electronics Co., A. Metz, C. Cole, K. Ito, S. Voronin, A. Ko, A. Ranjan, K. Kumar, TEL Technology Center, America, LLC

For advanced CMOS nodes, traditional patterning processes are challenged to meet the technology needs of certain key levels. For example, conventional 193nm immersion lithography is not able to resolve features below 40nm half pitch with a single exposure without severe design rule restrictions. Until further wavelength scaling through Extreme Ultraviolet (EUV) has matured, the industry's attention is focused on advanced patterning schemes such as Pitch Splitting (PS) Lithography and Sidewall Image Transfer (SIT). In PS, a pattern is defined by two lithography exposure with a certain coordinate shift between the two exposures. PS can be achieved through either litho-etch-litho-etch or litho-litho-etch. In SIT, a pattern is defined by creating a mandrel in one lithography exposure, depositing a conformal spacer film on the mandrel, and pulling out the mandrel, resulting in two standing spacer for the pattern frequency doubling. This work evaluated the advantages and technical challenges of PS and SIT patterning schemes for line-space application. We will focus on CD uniformity improvement, line edge/line width roughness control, pitch walk control, and the extendability of each technique. RIE challenges common to double patterning such as through pitch etch bias will also be discussed.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities and in joint development with TEL Technology Center, America, LLC

5:00pm MS+AS+EL+EM+PS+TF-TuA10 High Throughput Electrospinning of Ceramic Nanofibers, S. Sood, P. Gouma, State University of New York at Stony Brook (Stony Brook University)

High yield nanomanufacturing has been the focus of greater attention due to the emerging importance of functional nanomaterials. Electrospinning is a nanomanufacturing process that faces challenges as far as its scalability is concerned. Even the existing high-throughput electrospinning systems are limited to processing thin layers of polymer nanofibrous mats. Nanofibrous ceramics have rarely been studied with respect to their electrospinning processing. On the other hand, electrospun nanowires of ceramics are key to

nanotechnology and nanomedicine applications (e.g. electrospun MoO₃ nanowires have been used as ammonia sensors for application in non-invasive diagnostics [1]). In this study, the scalable synthesis of ceramic oxide nanomats by the multi-jet design that we developed and built and which enables very high yield of ceramic nanofibers is discussed. As a scaled up approach to traditional needle electrospinning [2], up to 24 jets are spun simultaneously using similar processing parameters as a traditional needle set up. Due to a thin metallic disc design, with tiny holes drilled at the disc, the electric field is evenly distributed to all jets. Continuous replenishment of the source disk at higher flow rates allows for high yields of nanofibers.

P. Gouma, K. Kalyanasundaram, and A. Bishop, "Electrospun Single Crystal MoO₃ Nanowires for Bio-Chem sensing probes", *Journal of Materials Research, Nanowires and Nanotubes special issue*, 21(11), pp. 2904-2910, 2006.

S. Sood, S. Divya, P. Gouma, "High throughput electrospinning of 3D nano fibrous mats". *Journal of Nanoengineering and Nanomanufacturing*. Accepted Publication. In Print, 2013.

5:20pm **MS+AS+EL+EM+PS+TF-TuA11 Manufacture and Characterization of Silver and Copper Nanorods Produced via Forcespun Nylon 6 Nanofibers Templates**, *D.M. Mihut, K. Lozano, W. Zhao*, The University of Texas Pan American

The Nylon 6 nanofibers are produced using the forcespinning method and further on coated with metallic thin films using the thermal evaporation equipment. The Nylon 6 nanofibers are used as templates in order to obtain silver and copper nanorods where the polymer is removed after high temperature calcination from the metallic coated structures. The metallic nanorods morphology and electrical behavior are characterized using the scanning electron microscopy, scanning transmission electron microscopy (SEM, STEM), energy dispersive X-ray spectroscopy (EDX) and electrical measurements. This method of fabrication offers the ability to obtain controlled ultrafine size metallic nanorods.

Plasma Science and Technology Room: 102 B - Session PS1-TuA

Plasma Diagnostics, Sensors and Control

Moderator: N.St.J. Braithwaite, The Open University, UK

2:00pm **PS1-TuA1 Real Time Feedback Control of Photoresist ashing in an Electron Cyclotron Resonance Plasma Chamber**, *B.J. Keville, C. Gaman, Y. Zhang, A.M. Holohan, S. Daniels, M.M. Turner*, Dublin City University, Ireland

Present practice in plasma-assisted semiconductor manufacturing specifies recipes in terms of inputs such as gas flow rates, power and pressure. However, ostensibly identical chambers running identical recipes may produce very different results. Extensive 'chamber matching', i.e. initial iterative, empirical tuning of the process recipe, which entails time-consuming, ex situ statistical analysis of process metrics, is required to ensure acceptable results. Once matched, chambers are run 'open loop' and are thus sensitive to disturbances such as actuator drift, wall seasoning and substrate loading, which may have deleterious effects on process metrics such as etch depth, uniformity, anisotropy and selectivity. An alternative approach, which may reduce sensitivity to disturbances of the plasma, would be to specify a recipe in terms of quantities such as active species densities, and to regulate these in real time by adjusting the inputs with a suitable multivariable control algorithm. Multivariable closed loop control of an SF₆/O₂/Ar plasma in an Electron Cyclotron Resonance (ECR) etcher is the focus of a major research program in the National Centre for Plasma Science and Technology (NCPST) in Dublin City University (DCU). As an intermediate step, real time control of an O₂/Ar plasma used for photoresist ashing has been implemented. More specifically, the oxygen 844 and argon 750 line intensities measured by optical emission spectrometry have been regulated by adjusting microwave power and oxygen flow rate in real time by means of a control algorithm. In order to test the efficacy of the control algorithm in reducing the sensitivity of the ashing rate to wall conditions, a wall disturbance was simulated by fluorinating the chamber walls using an SF₆ plasma prior to O₂/Ar ashing. In the open loop case, wall fluorination results in a large increase in the 844 line intensity, which is indicative of an increase in the density of atomic oxygen, and a concomitant increase in the ash rate is observed. However, under closed loop control, the average ash rate is unaffected by wall fluorination, thus demonstrating effective attenuation of the disturbance. Although this may not necessarily be of intrinsic interest – one generally ashes to end point without being overly concerned about tight control of the ash rate – it indicates that real time control of a plasma application – ashing, in this case – may be achieved

indirectly by control of active species in the plasma. This has important implications for applications where tight control of dimensions is critical – etch profile, for example.

2:20pm **PS1-TuA2 Diagnostics of Inductively-Coupled Plasmas in Hydrogen Bromide : Bromine Atom and Electron Densities**, *J.-P. Booth, N. Sirse, P. Chabert, M. Foucher*, LPP-CNRS, Ecole Polytechnique, France

Inductively-coupled plasmas (ICP) containing hydrogen bromide are widely used for conductor-etch applications, often using mixtures with Cl₂ and O₂. However, very few scientific studies (whether theoretical, simulation or experimental) have been made of HBr plasmas [1, 2] . We have studied pure HBr plasmas in an industrial-scale ICP (diameter 550mm, height 100mm, excited at 13.56MHz by a 4-turn planar coil) adapted for advanced diagnostic techniques.

We have demonstrated the first detection of Br atoms by two-photon laser-induced fluorescence (TALIF). The relative variation of Br atoms was determined as a function of HBr pressure (5-90 mTorr) and RF power (20-500W). The Br density increases with pressure over this range, although the dissociation fraction (Br density divided by the total gas pressure) decreases with pressure. The Br density also increases with RF power up to about 100W, but then progressively saturates. This saturation could be attributed to complete dissociation of the HBr, or to the onset of gas heating leading to gas density reduction. Measurements of the Br decay rate in the afterglow of a pulsed plasma allow the surface reaction coefficient of Br to be estimated.

The electron density was determined using a microwave hairpin resonator [3] . With HBr pressure the electron density peaks at 10 mTorr, and it increases with RF power. This behaviour is very similar to that observed in pure Cl₂, although the densities are about a factor 2 lower in HBr. The radial profiles of electron density are centre-peaked at low pressure, but at pressures above 50 mTorr the maximum is off-axis, peaking under the RF antenna coils.

This work was supported by Agence Nationale de la Recherche project INCLINE (ANR-09 BLAN 0019) and by the Applied Materials University Research Partnership Program. NS acknowledges the Ecole Polytechnique for a post-doctoral grant.

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[2] Sasic O., Dujko S., Makabe T., et al., *Chemical Physics*, 2012, **398**, 154-159

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2:40pm **PS1-TuA3 Ion Energy Distribution Measurements at the Substrate Location in Continuous-wave and Pulse Modulated Plasmas**, *D. Gahan, P. Scullin, D. O'Sullivan, M.B. Hopkins*, Impedans Ltd., Ireland **INVITED**

Low pressure plasmas are used extensively in modern industry to process substrates. Both etching and deposition processes are controlled by energetic ion bombardment of the substrate. As substrates become larger, feature sizes smaller and film properties more complex there is an increasing demand for accurate monitoring and control of the ion energy distribution. Ion energy measurements have been reported in the literature for many decades. The two most common instruments that have been used are the quadrupole mass spectrometer and the retarding field energy analyzer (RFEA). The simplicity of the RFEA has led to its widespread use in various applications. The focus of this talk will be on the recent advances in RFEA technology for ion energy measurements in different types of plasma processes. In most cases the substrate is processed using an electrical bias. The substrate holder may be powered with radio-frequency (RF), pulsed-RF, direct current (DC) or pulsed-DC electrical signals. This complicates the use of RFEAs for ion energy measurement at the substrate location. The presence of the RFEA must not disturb the electrical bias and the electrical bias must not impair the RFEA data acquisition. Here we present an electrically filtered RFEA technology that allows for deployment at the biased substrate location. The filtering allows the RFEA sensor to float at the electrical bias voltage. We will discuss a number of filter configurations that cover the many frequencies, waveform shapes and bias levels that can be encountered. We also discuss a special configuration that permits time resolved measurements of the ion energy at the biased substrates under certain conditions. A number of novel extensions to the standard technology will also be presented. Spatially resolved measurements of the ion energy at multiple locations (simultaneously) across 300mm and 450mm substrate holders, used for plasma etching, will be presented. This RFEA design gives important information about the spatial uniformity of the plasma process under various plasma conditions. An embodiment of the RFEA design which can be used to determine the ion

angular distribution is presented. This technique uses an additional orifice with variable aspect ratio to scan the angular distribution of the incoming ions across the energy range. Measurement of the ion angular distribution is particularly important near the edge of substrates, where yield is often poor due to sheath curvature in this region. Finally, the first results of a novel RFEA configuration that enables discrimination of the different ion species in the bombarding energy distribution will be presented and discussed.

4:00pm PS1-TuA7 Time-resolved Optical and Electrical Diagnostics of Pulsed Plasmas Etching Processes, G. Cunge, M. Brihoum, M. Darnon, E. Despiau-Pujo, A. Davydova, M. Haass, R. Blanc, Cnrs/ujf/ Cea - Ltm, France, N.St.J. Braithwaite, The Open University, UK, D. Gahan, Impedans Ltd, Ireland, S. Banna, AMAT, O. Joubert, N. Sadeghi, Cnrs/ujf/ Cea - Ltm, France

INVITED

Pulsed ICP plasmas are a promising solution to several issues related to IC fabrication. Recent results are indicating that pulsing the ICP power and/or the RF biasing power allows to increase the etch selectivity, to reduce plasma induced damages and to minimize ARDE. However, the reasons for these improvements remain unclear. In particular, the impact of plasma pulsing on the radicals flux, on the ion flux and on the ion energy in electronegative plasmas has not been studied in details. We have used a capacitively-coupled planar ion flux probe to monitor the time variations of the ions flux in an industrial ICP etch reactor from AMAT. At the same time, the time-averaged IEDF are measured by an RFA analyzer. Finally the radicals' densities are measured with a 10 μ s time resolution by combining several diagnostic techniques: small polyatomic radicals are detected by broad band absorption spectroscopy (BBAS) in UV with highly stable LEDs as a light source, large closed shell molecules are detected by BBAS in the VUV and atomic species are monitored by threshold ionization modulated beam mass spectrometry. We discuss in detail the experimental set-up that we have designed to carry out such time resolved measurements. Results are presented for various electronegative (Cl₂, BC1₃, SiCl₄, SF₆, CF₄) plasmas, that are synchronously pulsed (ICP and rf bias pulsed in phase) or in which only the rf bias power is pulsed. We will show that the duty cycle is the predominant parameter to control the ion flux, the ion energy and the plasma chemistry. These results are in good agreement with global models of electronegative Cl₂ plasmas. In particular, we show that in chlorine based plasmas, both the radical densities and the ion flux drops dramatically when the duty cycle is reduced. As a result for the same rf biasing power, the ion energy is much higher in pulsed plasma than in a CW plasma. By contrast, in a pulsed ICP without bias power the time averaged ion energy is bimodal, with the predominance of a very low energy peak (1-5 eV). Therefore, plasma pulsing allows to reach new domains of ion energy and radical fluxes, thereby extending the operating range of ICP reactor to that of CCP plasmas and downstream plasmas. This has interesting applications for ultrathin layer etching, ranging from graphene cleaning to metal gate and nitride spacer etching processes. Finally, both radical and ions flux oscillations in the kHz range are observed by time resolved diagnostics in pulsed plasmas. We will show that they are due to the propagation of acoustic waves in the reactor, with potentially interesting effect on the process uniformity.

4:40pm PS1-TuA9 Optical Emission and Langmuir Probe Diagnostics of CH₃F-O₂ Inductively Coupled Plasmas, E. Karakas, V.M. Donnelly, D.J. Economou, University of Houston

CH₃F plasmas, mostly with added O₂, are used in selective Si₃N₄ etching over Si or SiO₂. Despite their use, fundamental plasma studies in these gas mixtures are very scarce. In this work, optical and Langmuir probe diagnostics were employed to study inductively couple plasmas in CH₃F/O₂ gas mixtures. In 50% CH₃F/50% O₂ plasmas, the electron density increased linearly (0.7x10¹¹→2.7x10¹¹ cm⁻³) as power was increased 150-400W at 10 mTorr, but only weakly (1.7x10¹¹→2.7x10¹¹ cm⁻³) within the pressure range of 10-40 mTorr at 300W. The effective electron temperature representing the high energy tail of bi-Maxwellian EEPFs was nearly independent of power and pressure. The gas temperature increased from 400-900 K as a function of inductive mode power between 75 and 400 W at 10 mTorr. For a constant feed gas flow rate and composition, the absolute H, F and O atom densities, estimated by optical emission rare gas actinometry, increased linearly with power. The feedstock gas was highly dissociated and most of the fluorine and oxygen was contained in reaction products HF, CO, CO₂, H₂O and OH. Reaction mechanisms were proposed to explain the observed behavior of the relative density of F and HF vs. power and pressure. Measured relative densities as a function of O₂ addition to CH₃F/O₂ changed abruptly for H, O, and particularly F atoms (factor of 4) at 48% O₂. A corresponding transition was also observed in electron density, effective electron temperature and gas temperature, as well as in C, CF and CH optical emission. These abrupt transitions were attributed to the reactor wall reactivity, changing from a polymer-coated surface to a polymer-free surface, and vice-versa, as the O₂ content in the feed gas crossed 48%.

*Work supported by Lam Research Corp.

5:00pm PS1-TuA10 Non-contact Measurements of Substrate-Temperature by Frequency-Domain Low-Coherence Interferometry, T. Tsutsumi, Nagoya University, Japan, T. Ohta, Meijo University, Japan, K. Ishikawa, K. Takeda, H. Kondo, M. Sekine, M. Hori, Nagoya University, Japan, M. Ito, Meijo University, Japan

High-precision, rapid temperature measurements on wafers such as silicon, sapphire, etc. are required for plasma processing. A method is demonstrated here that uses a frequency-domain low-coherence interferometer (FD-LCI).

In order to realize the plasma processing with high precision, the temperature control of wafer or chamber-wall is one of important factors. Especially the wafer temperature influences on etched profile and etching rates. Moreover, a spatial distribution of radicals in gas phase or plasma-surface interactions on the surface are affected by temperatures of the chamber-wall. Therefore, the precisely non-contact temperature-measurement technology is needed for the fabrication of electric devices.

In this study, we have developed a highly precise and non-contact temperature monitor using a Fourier domain low-coherence interferometer (FD-LCI) and a super luminescent diode (SLD: center wavelength: 1330 nm, spectral width: 37.6 nm) as a low coherence light source. The FD-LCI can measure an optical path length of wafer on the basis of auto-correlation signals, which are generated by interferences between the light reflected from the front and back surfaces, and analyzed by the inverse Fourier transform of spectral interferogram. Since the optical path is changed by thermal expansion and refractive-index, the wafer-temperatures can be analyzed. By this method, we have successfully achieved to estimate a temperature of various commercial wafers such as silicon, sapphire during plasma processes.

5:20pm PS1-TuA11 Detection of Vacuum Ultraviolet in Argon-containing Inductively Coupled Plasmas, S.B. Radovanov, Varian Semiconductor Equipment, Silicon Systems Group, Applied Materials Inc., H.M. Persing, Applied Materials Inc. Varian Semiconductor Equipment, Silicon Systems Group, Applied Materials Inc., J.B. Boffard, C.L. Culver, S. Wang, C.C. Lin, A.E. Wendt, University of Wisconsin-Madison

The spectrum of light emitted by plasmas used in materials processing applications includes vacuum ultraviolet (VUV) photons, which are known to play a significant role in critical surface reactions under certain process conditions. Monitoring of the surface flux of VUV photons emitted from the inductively coupled plasma (ICP) and its dependence on discharge parameters is thus highly desirable. However, non-invasive direct detection of VUV photons is generally difficult, as few window materials transmit in the VUV. We thus examine the argon resonance level atom concentration as a prospective proxy for VUV emission, as 106.7 and 104.8 nm VUV photons are produced in the spontaneous radiative decay from Ar resonance levels to the ground state. Argon resonance level concentrations have been measured in the center of an ICP with a planar spiral induction antenna through "branching fraction" analysis of the visible optical emission (OES) spectrum.* Measured concentrations are subsequently used as inputs to a VUV radiation transport model developed to determine the corresponding axial VUV photon flux. Reabsorption of VUV photons by ground state atoms is significant even at pressures as low as 1 mTorr, and a proper accounting in the model thus requires accurate representation of the gas temperature. Model results based on the resonance level concentrations over a range of pressures (1-25 mTorr) and RF (13.56 MHz) power (up to 1000 W) compare favorably with the axial VUV photon flux sampled directly through a small hole at the center of an electrode located opposite the ICP antenna. Absolute VUV fluxes were measured with a windowless aluminum oxide photodiode sensitive to wavelengths below ~110 nm. Additionally, relative VUV fluxes were also obtained using a sodium salicylate coating on the inside of a side port vacuum window. The sodium salicylate converts VUV into a detectable visible light signal through fluorescence, and, unlike the photodiode, is sensitive in the wavelength range of H atom VUV emissions (122 nm). Preliminary results suggest that a combination of photodiode and sodium salicylate signals thus allows discrimination between hydrogen and argon contributions to the VUV flux in Ar/H₂ gas mixtures.

Support from NSF grant PHY-1068670 and the Applied Materials Corporation is gratefully acknowledged.

*Plasma Sources Sci. Technol. **18** (2009) 035017.

5:40pm PS1-TuA12 Time-resolved In Situ Quantum Cascade Laser Diagnostics Applied to Transient Molecular Plasmas, S. Welzel, Eindhoven University of Technology, Netherlands, F. Brehmer, Eindhoven University of Technology, Netherlands; AFS GmbH, Germany, M.C.M. van de Sanden, Eindhoven University of Technology; DIFFER, Netherlands, R. Engeln, Eindhoven University of Technology, Netherlands

The detection of stable and transient species along with gas temperature measurements remains a challenge for the majority of molecular (complex) plasmas. Considering particularly plasmas at atmospheric pressure with

inherently small discharge volumes, (optical) access to the active plasma is often hampered. On the other hand, phase- and time-resolved *in-situ* measurements are a valuable tool (i) to establish heavy particle temperatures, (ii) to identify excitation mechanisms in the plasma, (iii) to discriminate gas phase and surface reactions as they occur on significantly different time scales, and (iv) to unravel particularly temperature-dependent reaction mechanisms. Modern mid-infrared laser sources, known as quantum cascade lasers (QCLs), provide a means for highly time-resolved absorption spectroscopy in the molecular "fingerprint" region. The time-resolution can be thereby as good as a few tens of nanoseconds. Although continuous-wave QCLs are increasingly being applied for conventional monitoring purposes, pulsed distributed feedback QCLs are perfectly suited for diagnostic studies on transient plasmas.

CO₂ containing dielectric barrier discharges (DBDs) operated in the mid-frequency (kHz) range were studied by means of *in-situ* time-resolved QCL absorption spectroscopy. Special beam shaping optics was used to accommodate the laser beam diameter to typical gap widths of ~ 1 mm in single and multiple-pass configuration. Different synchronisation schemes were applied to achieve phase-resolved measurements during individual AC cycles as well as to monitor molecular absorption signals during pulsed discharge operation. Mixing ratios of CO in its electronic and vibrational ground state were of the order of a few percent and thus confirmed earlier *ex-situ* studies of the effluent. More importantly, the concentrations levels were changing only slowly in time, i.e. of the order of the residence time. A direct CO₂-to-CO dissociation through electron impact appears very unlikely under these conditions. The kinetics of low-lying ro-vibrational states of CO₂ along with the evolution of the CO concentration were studied on a sub-millisecond time-scale to (i) establish (rotational) gas temperatures, and (ii) to estimate the influence of vibrational-vibrational and vibrational-translational energy transfer processes.

Plasma Science and Technology

Room: 104 C - Session PS2-TuA

Deep Etch Processes for Vias, Trenches and MEMS

Moderator: A. Agarwal, Applied Materials Inc.

2:00pm **PS2-TuA1 Plasma Deep Etching of Silicon, Titanium and Gallium Nitride for Microtechnology**, R. Dussart, GREMI CNRS/Université d'Orléans, France **INVITED**

Plasma deep etching is a necessary process step for the fabrication of most of microelectronic components, especially in power microelectronics and in MEMS technology. Although several etching processes were developed for silicon, deep etching of other materials such as titanium and gallium nitride is also of interest for innovative microdevices.

In this paper, deep etching of silicon using the so-called cryogenic process will be presented and compared with other processes. We will show and explain our characterization experiments by mass spectrometry, ellipsometry and *in-situ* XPS, which were carried out to investigate physical and chemical mechanisms involved in the silicon cryoetching process. These results were also used to develop the so-called STiGer cryoetching process, which will be also introduced. This particular process offers some advantages of the standard cryogenic process and is more robust.

Titanium deep etching using both fluorine and chlorine based chemistries was investigated by our group. Titanium is particularly interesting for bio MEMS applications. We developed the so-called APETi process to avoid roughness and increase the etch rate. With this process, we were able to etch up to 300 µm deep ring structures.

Finally, we will also show our process capabilities for deep GaN etching. For this material, a chlorine based chemistry is necessary to form volatile species. Measurements by Langmuir probe, by optical emission spectroscopy and by mass spectrometry were carried out to characterize the plasma in the different tested conditions. We will show that the material of the coverplate can play an important role in the etching mechanisms. Three types of defect were observed: « cavity » defects, « columnar » defects and the « white GaN ». The appearance mechanisms of these defects were studied and will be explained. Although we showed, by Transmission Electron Microscopy analysis, that the two first types of defect are clearly linked to intrinsic defects of the material itself, it is still possible to avoid their appearance during the etching.

2:40pm **PS2-TuA3 Simulation of Bosch Process Deep Silicon Etching - A Multi-scale Approach**, A. Pateau, A. Rhallabi, M.C. Fernandez, Université de Nantes, France, M. Boufnichel, F. Roqueta, STMicroelectronics Tours SAS

Deep etching of silicon is a very used process in the semi-conductor industry. Such high aspect ratio etchings can be obtained using Bosch process. This plasma process consists in alternating many etching and deposition steps at high etch rate (few seconds each). Two gases are mainly used: SF₆ for the etching step and C₄F₈ for the passivation.

To predict the silicon etch profile through the mask, we have developed an etching Bosch simulator. It permits to investigate plasma/surface interactions for both the deposition and the etching step. Based on a multi-scale approach the silicon etching simulator is composed of three modules: plasma, sheath and surface models. This allows to predict the etch profile as a function of the operating conditions (pressure, power, gas flow rates, time steps for deposition and etching cycles).

The plasma module is based on a global kinetic model which allows the calculation of the neutral and ion densities and fluxes as well as the electronic temperature and density using the machine parameter of the ICP reactor as input parameters.

The sheath module is based on the Monte-Carlo technique to calculate the Ion Angular and Energetic Distribution Functions (IAEDFs). Positive ion fluxes and electronic temperature and density calculated from de plasma module are used as input parameters in the evaluation of average sheath thickness and proportion of each considered positive ion.

The fluxes of neutral and ion species calculated from the plasma module and the IAEDF calculated from the sheath model are introduced as input parameters in the surface model. This model is based on the cellular Monte-Carlo method to describe the 2D etch profile through the mask and evaluate the etch rate evolution with time. Both the silicon substrate and the mask are discretized in uniform cells named super-sites. Each super-site contains a number of real atomic silicon sites which depends on the cell size. In our etching simulations, 1nm by 1nm cells are considered. This allows a good compromise between computing time and spatial resolution. The particles used are atomic fluorine for the reactive etching, atomic carbon, CF and CF₂ for the passivation polymer growth, and positive ions for the sputtering.

The simulation results show the influence of the input Bosch process parameters (RF powers, pressure, gas flow rates, time steps for deposition and etching cycles and bias voltage) on the etching processes like the etch rate and the deep etch profile evolution with etch time. Such an etching simulation tool can contribute to improve the deep silicon etching processes in terms of anisotropy and scalloping reduction.

3:00pm **PS2-TuA4 Titanium Deep Etching for Medical Applications**, T. Tillocher, P. Lefaucheur, GREMI CNRS/Université d'Orléans, France, B. Boutaud, Sorin Crm, France, R. Dussart, GREMI CNRS/Université d'Orléans, France

Titanium is a biocompatible material which is of great interest in the biomedical field and more especially for bio-MEMS, which have emerged recently. The fabrication of Ti platform based devices is adapted from micromachining techniques derived from microelectronics technologies. Most of the research work reported in the literature relies on a Cl₂/Ar chemistry to deep etch titanium, using masks like TiO₂, Ni or even SU8. Processes are performed at room temperature of the substrate with typical etch rates close to 1 µm/min. They provide rather smooth surfaces.

We report here the performances of deep titanium etching with SF₆ and Cl₂ based chemistries in an ICP etching tool. Samples are pieces of a patterned titanium wafer glued on a silicon carrier wafer. Mask is a 5 µm thick nickel layer.

Our preliminary results have shown that either a SF₆ plasma or a Cl₂/Ar plasma can be used separately to etch titanium. A SF₆ plasma helps to reach etch rates as high as 4 µm/min at higher pressures (a few Pa) but profiles are isotropic. A Cl₂/Ar chemistry at low pressure (almost 1 Pa) is preferred to get vertical sidewalls but the etch rate is reduced. This is why we proposed to mix these two chemistries to increase the etch rate while keeping vertical sidewalls. However, this process is not reproducible in our conditions since, in most cases, it leads to a very high roughness and a drop in the etch rate.

This non-reproducibility may be due to the use of a silicon carrier wafer: SiCl_x species, coming from the etch by-products of the silicon wafer, may participate to one passivation layer growth on the Ti surface as well as the chamber walls. This induces a micro-masking effect which subsequently leads to the formation of an unwanted roughness.

A SF₆ plasma appears to be a good way to remove (at least partially) the layer inducing roughness, which hence leads to a better reproducibility. As the process presented previously already contains SF₆, but is not reproducible, this means that the balance between etching and deposition becomes favorable to deposition from one process to another. This is why both the SF₆ injection and the whole process have been optimized to

overcome this issue. It was then possible to etch 300 μm of Ti within nearly 3h30. Consequently, 300 μm have been etched with an average etch rate of 1.4 $\mu\text{m}/\text{min}$. The slope is slightly negative on the first half of the ring and tends to be more isotropic on the second half. A significant undercut can also be observed (a few 10s of μm). The estimated selectivity to the nickel mask is 35. The process has been repeated many times and the profiles were always reproducible, which is a significant improvement.

4:00pm PS2-TuA7 Selection of non-PFC Chemistries for Through-Silicon via Etch, *K. Chen, T. Kim, J.P. Chang*, University of California at Los Angeles

The continued extension of Moore's Law, which dictates that the density of integrated circuit (IC) devices doubles every two years, presents formidable challenges in realizing complex and three-dimensional interconnect structures. Through-silicon-via etch (TSV) is at the core of 3-D integration, which yields higher performance than conventional 2-D wiring systems, and has been demonstrated with Bosch deep reactive ion etching (DRIE), cryogenic DRIE, laser drilling, and wet etching. In order to achieve the desired and continuously increasing aspect ratio (AR) of the features required for the device integration, DRIE is the preferred method for TSV for the attainable vertical sidewalls and high AR. Unfortunately, the primary gases used in DRIE for TSV are SF_6 and perfluorocarbon (PFC) gases, which are high global warming potential (GWP) greenhouse gases, making their increased usage undesirable.

In this work, a thermodynamics approach is used to assess and select other viable etch chemistries for TSV that are non-PFC, in an effort to reduce the usage of PFC gases and minimize their environmental impact. A systematic study is based on the assessment of various halogen-based gases, utilizing a volatility diagram where the partial pressure of the etch products are determined as a function of the etchant pressure at various temperatures. This functional relation can be determined from the thermodynamic equilibrium between the surface and gas-phase species, by considering the standard Gibbs free energy and the equilibrium constant. A careful control of the etchant partial pressure near the isomolar point, where the partial pressure of the volatile species would reach that of the equilibrium value, has been shown to be necessary to control the formation of volatile species. Amongst various candidates, NF_3 , a non-PFC gas with greenhouse rating only 1/100th in atmosphere, appears promising. From the thermodynamics analysis, the generation of fluorine atom from SF_6 and NF_3 is comparable, however, NF_3 is much more able to form more SiF_4 , the volatile etch product, than SF_6 . While this is promising, another significant reaction product from NF_3 is Si_3N_4 , which is non-volatile. The addition of a second chemical such as O_2 can necessitate its subsequent removal, through the formation of volatile products such as nitrogen oxides (N_xO_y). In addition, NF_3 is also capable of removing SiO_2 which is unintentionally formed during reaction with O_2 . This work will highlight the analysis to design a NF_3/O_2 process (sequential exposure versus mixture) that yields comparable etch results compared to that achieved by SF_6 , thereby offering a viable alternate for TSV etch.

4:20pm PS2-TuA8 Sub-22nm Node Mask Patterning for Deep Silicon Trench Etch, *B. Avsarala, S. Lefevre, V. Chakrapani, H. Haga, H. Matsumoto, Q. Yang, Y. Chiba, A. Ko, A. Selino Jr., K. Kumar, P. Biolsi*, TEL Technology Center, America, LLC, *F.L. Lie, I. Saraf, S. Kanakasabapathy*, IBM

The fabrication of ever smaller feature sizes at increasing density has driven more stringent requirements on photolithographic processes and patterning schemes. In the sub-22nm DRAM technology, the fabrication of deep silicon memory cells at aspect ratios greater than 30 ratio (depth > 3 μm : critical dimension < 0.1 μm) is enabled by a complex mask assembly. In this paper, we will discuss RIE process development for patterning the mask assembly as well as the high aspect ratio Si trenches. The mask assembly comprises of a photo resist layer, silicon anti-reflective coating, organic planarizing layer, oxide layer, and nitride layer deposited on top of a Silicon-on-Insulator (SOI) substrate. Achieving a vertical profile along the trench and across different material types of the mask, while still maintaining the required critical dimension, are major challenges in patterning the mask assembly. The verticality of the different layers in the mask assembly is key because it subsequently affects the deep Si etch process. We will discuss the challenges in achieving high aspect ratio Si trench and key process parameters that influence its dimensions. The paper also describes the capabilities of a commercially available Capacitively Coupled Plasma reactor to meet the requirements of these advanced complex film stacks.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Semiconductor Research and Development teams in Albany & Hopewell Junction, NY

4:40pm PS2-TuA9 Reduction of Aspect Ratio Dependency in Silicon Trench Etch, *R.L. Bates*, University of Texas at Dallas

The etch rate of deep features in silicon, such as trenches and vias, can vary significantly with the changing aspect ratio of the feature. Developing a better understanding of the complex volumetric and surface chemistry as well as the etching mechanisms controlling the Aspect Ratio Dependent Etch-rate (ARDE) continues to present research opportunities. Recall that ARDE is generally characterized by small AR features etching at faster rates than large AR features. The main causes of ARDE include Knudsen transport of neutrals into and out of the features as well as ion loss to the walls due to angular spread in the velocity distribution function and differential charging of insulating microstructures [1]. This work focuses on using a continuous plasma process utilizing a gas mixture of $\text{SF}_6/\text{C}_4\text{F}_8/\text{Ar}$ to produce trenches of varying widths and depths. The experimental results were obtained using a Plasma-Therm Versaline processing system. Experiments were performed to show that the etch rate of low AR features can be reduced through the deposition of a passivation layer and thereby allow larger AR features to catch up. It is also possible to invert the ARDE in certain circumstances. We will present the insights we have gained into the ARDE process and the solution we have tested. [1] R. Gottscho & C. Jurgensen, *J. Vac. Sci. Tech. B*, **10**, 2133, (1992). This research was supported through SRC Award: 2012-VJ-2261. The authors thank the staff of the UTD clean room (G. Pollack, S. Riekema, B. Albert) for their gracious assistance in processing and measuring these samples.

5:20pm PS2-TuA11 Reaction Mechanism at the Sidewall of Through Si via (TSV) Etching by $\text{SF}_6/\text{O}_2/\text{SiF}_4$ Plasma, *I. Sakai*, Toshiba Corporation, Japan, *S. Amasaki, T. Takeuchi, K. Takeda, K. Ishikawa, H. Kondo, M. Sekine*, Nagoya University, Japan, *N. Sakurai, H. Hayashi, T. Ohiwa*, Toshiba Corporation, Japan, *M. Hori*, Nagoya University, Japan

One of the key processes for 3D-LSI is through Si via (TSV) formation. To form large and deep via holes through a wafer, a high etch rate deep etching technology using SF_6/O_2 plasma has been developed [1]. It is reported that high etch rate is obtained by supplying a large amount of F radicals and the etch profile is controlled by forming an oxidized layer as an etch inhibitor on the TSV sidewall. In the previous study [2] we showed that, as a result of competitive reaction of etching and oxidation by F and O radicals, even at the 75% O_2 addition condition Si etching by F radicals is confirmed. In this study, we aimed to suppress sidewall etching further by addition of SiF_4 gas to SF_6/O_2 plasma, and examined its effect by analysis of the Si surface.

Si wafer was placed on a grounded electrode at the remote plasma region of a 500 MHz ultra high frequency plasma reactor. We assumed that the influence of ions was small and radical reaction dominant, so we could simulate the reactions at the sidewall of TSV RIE. The process gas chemistries used were SF_6/O_2 and $\text{SF}_6/\text{O}_2/\text{SiF}_4$.

The Si etch depth dependence of $\text{SF}_6/\text{O}_2/\text{SiF}_4$ plasma etching on O_2 gas addition was examined. The etch depth of Si after 3 min plasma exposure was measured from SEM images of 8 μm square hole patterned Si wafers with 2 μm thick SiO_2 as mask. Etch depth decreased with SiF_4 addition. For example, at 75% O_2 addition, the etch depth was about 0.25 μm , 1/4 of that without SiF_4 addition. Etch depth dependence on O_2 flow rate ratio showed a decreasing trend, same as that without SiF_4 addition. At 90% O_2 gas flow rate ratio, etching stopped and thickness increased, indicating that film was deposited on the Si surface. The thickness of the etch-inhibiting reaction layer including Si, F, O (SiOF film) was calculated from the Si2p spectra of XPS after 1 min plasma exposure. Thickness increased with O_2 addition, and especially when the O_2 flow rate ratio was more than 75% in the case of $\text{SF}_6/\text{O}_2/\text{SiF}_4$, it became profoundly thicker, more than 8.7nm. It is speculated that reaction of O radicals and SiF_4 occurred on the Si surface and etching was suppressed by Si atoms supplied from the plasma in addition to the inhibiting effect of the SiOF formation. Finally, the F/O ratio of the SiOF layer at the Si surface was calculated from the peaks of F1s and O1s. Under this experimental condition, it was found that the ratio was constant, about 2, regardless of O_2 gas flow rate ratio, which is similar to the previous result without SiF_4 addition.

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Plasma Science and Technology

Room: Hall B - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Dry Deep Etching of GaN Wide Band-gap Semiconductor. *N. Gosset*, GREMI CNRS/Université d'Orléans, France, *J. Ladroue*, STMicroelectronics Tours SAS, France, *T. Tillocher*, *P. Lefaucheu*, GREMI CNRS/Université d'Orléans, France, *M. Boufnichel*, STMicroelectronics Tours SAS, France, *R. Dussart*, GREMI CNRS/Université d'Orléans, France

Gallium nitride (GaN) is a III-V semiconductor with a large and direct band-gap (3.4 eV). Furthermore, GaN has a high electron mobility and strong chemical bonds. These physical properties make GaN very interesting and open new prospects for microelectronics power devices. Indeed, GaN-based devices, compared to silicon devices, can operate under high temperature, high power and high frequency. For GaN-based power devices, an etched depth as high as 6 to 10 μm is typically required. This is considered as deep etching compared to the etch depth necessary for light emitter devices (a few hundred nanometers). It was shown that wet etching of GaN c-plan (plan where etching is generally needed) is limited due to its chemical inertness. Therefore GaN deep etching is achieved by plasma etching. Chlorine-based chemistries are commonly used because GaCl_3 is the most volatile Ga etching product. We studied GaN etching (7 μm thick epilayer grown on Si) in Cl_2/Ar plasma using two industrial Inductively Coupled Plasma (ICP) reactors (Corial 200IL and Alcatel 601 E) and by Ion Beam Etching (IBE) (Plassy MU450). After etching, three regimes of defects were observed: columns, pits and "White GaN". It was shown that both columns and pits are linked to nanopipes and dislocations created during epitaxial growth of GaN. In addition, oxygen based species, coming from either the SiO_2 coverplate or the alumina/quartz tube, play an important role in the columnar regime. They preferentially oxidize dislocations, leading to the observed columns. "White GaN" is a very high roughness coming from surface over-oxidation. For industrial applications, all these defects and roughness must be limited. Plasma investigations, using Langmuir probe, mass spectrometry and optical emission spectroscopy, revealed that SiCl_4 can scavenge oxygen. This subsequently results in elimination of defects. Consequently, using Si coverplate or injection of SiCl_4 leads to defect free surfaces. An optimized IBE process appears to be also a way to reduce defects. The addition of other gases (like BCl_3 , CHF_3 and SF_6) will be also investigated to evaluate the impact on both GaN etch rate and selectivity in Cl_2/Ar chemistry. XPS and AFM surface analysis will be performed to better understand the formation mechanism of defects. Finally, regardless of defects, etch rate as high as 1 $\mu\text{m}\cdot\text{min}^{-1}$ and a selectivity of 6 can be obtained.

PS-TuP8 Fluorocarbon Films Deposited by c-C₄F₈/N₂/Ar Plasmas: The Effect of N₂-addition on Gas Phase Kinetics and Surface Chemistry. *P.K. Kao*, National Taiwan University, Taiwan, Republic of China, *P.J. Kuo*, *P.W. Chiou*, *C.C. Chou*, Tokyo Electron Taiwan Limited, Taiwan, Republic of China, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Fluorocarbon films deposited using c-C₄F₈/N₂/Ar capacitively coupled plasmas are studied with the goal of understanding the effects of N₂-addition on surface chemistry. The plasma system used is a parallel-plate discharge sustained by a 13.56 MHz power source with the electrode diameter 25.4 cm and a gap distance 6 cm. Quartz crystal microbalance (QCM), Fourier transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), and contact angle measurement are used to characterize the film properties. QCM measurements show a monotonically increase in the deposition rate with N₂ addition, suggesting that CN_xF_y deposition rate surpassed the rate of forming volatile species. FTIR spectra show an additional adsorption near 1350 cm^{-1} for conditions with N₂ addition. This can be caused by either the incorporation of nitrogen into the polymer chain or by creation of additional disordered sp² carbon in the film. The XPS C_{1s} spectrum of the film shows four major peaks, assigned to CF_x ($x = 1, 2, 3$) and C-CF bonds. With N₂ admixture, CFN bonds appear in the C_{1s} spectrum, while the amount of CF_3 and CF_2 bonds only decrease slightly. In support of the XPS data, the water contact angle on FC films remains 100–110° and does not change noticeably with N₂-addition. At the end of the presentation, the process significance in N₂ addition into c-C₄F₈/Ar/N₂ plasmas will be discussed.

PS-TuP11 Etching Characteristics of AlGaIn and GaN in Inductively Coupled Cl₂ Plasma. *J. Cao*, *Y. Lu*, *R. Kometani*, *J. Park*, *K. Ishikawa*, *K. Takeda*, *H. Kondo*, *M. Sekine*, *M. Hori*, Nagoya University, Japan

Gallium nitride and related alloys have been expanding their applications for next-generation optoelectronics such as HEMTs or white LEDs. Plasma etching processes are necessary especially for ternary compounds such as AlGaIn and InGaIn. To control precisely profiles at nano-scale and to reduce plasma-induced damages, which influencing the device performance,¹⁻³ the mechanism of reaction of ions and radicals in plasma with surfaces should be clarified. In this research, we investigated the etching mechanism of AlGaIn in chlorine plasma with focusing on surface stoichiometric composition.

Samples were Al_{0.32}GaN, Al_{0.47}GaN and GaN epitaxial films grown on Si substrate. Photolithographic patterning of UV photoresist was conducted. After chemical cleaning, an inductive coupled plasma etcher was used; the typical condition is antenna power of 200 W, bias RF power of 0 - 120 W, Cl₂/Ar mixture gas flow rate of 30 sccm at 1 Pa. The samples were checked electrostatically on the stage kept at room temperature. X-ray photoelectron spectroscopy (XPS) was used for stoichiometric composition analysis.

When changing the ratio of Cl₂/(Cl₂+Ar) from 0 to 100%, the etch rate of GaN and AlGaIn was increasing with the Cl₂ ratio. The etch rate in all cases saturated as increased the Cl₂ flow ratio above 40%. Order of the etch rate among the films were Al_{0.47}GaN < Al_{0.32}GaN < GaN, which could be explained by their sputtering threshold energies for Al-N of 11.52 eV and Ga-N of 8.92 eV.⁴ Since the etching products such as AlCl_x have high volatility compared with GaCl₃, a layer consisting of low Al-to-Ga ratio was possibly formed on the AlGaIn surface. We will discuss the effects of plasma parameters on both etching profiles and surface stoichiometry in order to elucidate comprehensively understanding of the etching mechanism.

This work was supported by the Knowledge Cluster Initiative (Second Stage), MEXT, Japan. We would like to thank Taiyo Nippon Sanso Corp. for sample preparations.

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PS-TuP12 Selection of Materials and Surface Finishes for Reduced Particle Formation Upon Ion Beam Bombardment in EUV Mask Blank Production Devices. *A.M. Lietz*, *D. Curreli*, University of Illinois at Urbana Champaign, *A.V. Hayes*, *A. Devashayam*, Veeco, *D.N. Ruzic*, University of Illinois at Urbana Champaign

Extreme UltraViolet Lithography (EUVL) requires reflective mask blanks, manufactured by ion beam sputtering a multilayer stack of thin films, primarily Mo and Si, onto a mask substrate. At least 40 bilayers of Mo and Si are necessary to produce a surface which has sufficient EUV light reflectivity for use in high volume manufacturing exposure tools. When contaminant particles deposit between these layers, the EUV light is absorbed or scatters irregularly, rendering the mask blank unusable. One possible source of such particles is bombardment of shields in the deposition chamber by energetic particles scattered from the ion beam and target and "overspill" of the tails of the ion beam off the edge of the target under oblique target angle of incidence. Shields are used to cover targets that are not in use and prevent deposition or sputtering nearby surfaces and equipment. These shields must be able to accept many successive layers of deposition without flaking and forming particles of deposited material. They must also be able to withstand ion beam overspill bombardment, while forming a minimal amount of particles.

In order to evaluate improved shield materials and surface finishes, shield samples were placed under a broad angle ion beam and particles were collected on a witness plate. Shields of various materials and surface finishes were compared to determine the lowest level of particle formation. The total number of particles on the witness plates was quantified using laser scattering particle detection. Particle sizes and shapes were quantified with high resolution SEM imaging of the witness plate, and their composition was determined using backscattered electron imaging. The shield samples themselves were also analyzed using SEM to check for qualitative features, such as plateau formation, that may indicate the mechanism of particle formation.

PS-TuP13 The Influence of Plasma and Vacuum Ultraviolet Radiation on the Time-Dependent Dielectric Breakdown of Porous Low-k Dielectric Films, D. Pei, M. Nichols, H. Sinha, University of Wisconsin-Madison, S. Banna, Applied Materials Inc., Y. Nishi, Stanford University, J.L. Shohet, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDDB) is a major concern for low-k dielectrics. The TDDB properties of porous organosilicate glass (OSG) and photopatternable low-k dielectric (PPLK) films after plasma and/or VUV exposure are evaluated using constant voltage time-to-breakdown measurements. To examine the effect of plasma exposure on TDDB degradation, dielectric films were exposed to Ar plasma in an ECR reactor. To separate the effect of vacuum ultraviolet (VUV) radiation on TDDB from charged particle bombardment, synchrotron radiation was used. This also has the advantage of being able to vary the wavelength of the radiation continuously. Dielectric films were exposed under different photon energies with the same fluence. After plasma or VUV exposures constant-voltage time-to-breakdown measurements were made for each sample. Weibull statistics were used. Both the results from PPLK and OSG showed that when the samples were exposed to plasma, significant degradation in breakdown time was observed. The VUV radiation under different photon energies shows less effect on the TDDB of both PPLK and OSG for the same fluence as the plasma. Charge-to-breakdown measurements also show similar results.

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PS-TuP14 Noninvasive, Real-Time Measurements of Plasma Parameters via Optical Emission Spectroscopy, S. Wang, J.B. Boffard, C.C. Lin, A.E. Wendt, University of Wisconsin-Madison, S.B. Radovanov, H.M. Persing, Varian Semiconductor Equipment, Silicon Systems Group, Applied Materials Inc.

Plasma process control applications require acquisition of diagnostic data at a rate faster than the characteristic time scale of perturbations to the plasma. Diagnostics based on optical emission spectroscopy (OES) of intense emission lines permit rapid noninvasive measurements with low-resolution (~1nm), fiber-coupled spectrographs, which are included on many plasma process tools for semiconductor processing. The use of OES is an established practice to determine when a process is completed, i.e., the process "endpoint," by detecting changes in intensity in optical emissions of key gas-phase chemical species, and OES can also be used to detect the presence of impurities and monitor changing reactor wall conditions. More detailed real-time information about the plasma state is increasingly desirable for process monitoring, however, due to progression in the semiconductor industry toward plasma processes with both tighter tolerances and multiple steps, i.e., where operating parameters are varied over the course of the process. In this work,* we examine the utility of plasma optical emissions from argon measured with a low-resolution spectrograph (Verity 1024 SH) as a real-time monitor of plasma parameters during the course of a plasma process, based on a rapid method to monitor and analyze the intensities of a select group of Ar emission lines to dynamically determine the following plasma parameters. Electron temperature and density are relevant parameters for characterization of the dynamic behavior of processing plasmas, because gas phase reactions are driven by collisions involving energetic plasma electrons. Metastable and resonance level concentrations are also relevant as these species play significant roles in plasma processing, through energy released when they de-excite upon reaching substrate surfaces, and through the emission of VUV photons which enhance surface reactions. These parameters are unambiguous indicators of the instantaneous plasma state and as such may play a valuable role as monitors for closed-loop process control. Results will be presented for argon and argon/mixed-gas (Ar/N₂, Ar/O₂, Ar/H₂) inductively coupled plasmas. Accuracy of the results (which are compared to measurements under static conditions made by Langmuir probe and white-light absorption spectroscopy) are typically better than ±15%. The system time resolution is ~0.1 s, which is more than sufficient to capture the transient behavior of many processes, limited only by the time response of the spectrograph used.

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PS-TuP16 80 MHz Capacitively Coupled SiH₄/H₂ Discharge for m-Si Thin Film Deposition - 2 Dimensional Fluid Model Simulation, H.B. Lin, S.E. Lien, C.H. Hsieh, K.C. Leou, National Tsing Hua University, Taiwan, Republic of China, C.C. Hsieh, C.F. Ai, Institute of Nuclear Energy Research, Taiwan, Republic of China

Capacitively coupled SiH₄/H₂ plasmas (CCP) have been widely employed for deposition of Si film for applications such as thin film transistors and

thin film solar cells. For Si thin film solar cells, requirements for yielding higher conversion efficiency at a lower cost calls for a high rate and high uniformity plasma process for deposition of microcrystalline silicon (m-Si) film. A better understanding of the plasma discharge is needed. In this study, a 80 MHz SiH₄/H₂ CCP discharge has been investigated by numerical simulation based on fluid model, with 27 species and 47 reactions. Simulation results show that plasma density, as well as the number densities and fluxes of H, SiH₂, and SiH₃, important reactive species for the growth of m-Si film, as well as the ratio of H/SiH₃ flux, a key indicator for crystal fraction of m-Si film, increase with rf power, as expected. Compared with the case in 27.12 MHz, the results also show that plasma density for the 80 MHz discharge are higher, due to frequency effect in the dominate electron heating mechanism, and, consequently, the densities of the key radical species also drop. More importantly, the ratio of H/SiH₃ flux is also higher for the 80 MHz cases. Further more, the plasma potential, which determines the energy of ions incident on the grounded substrate electrode, decreases as operation frequency decreases. Consequently, a higher crystal fraction can be obtained by increasing the frequency of the rf power of plasma reactors, due to less damage on films causes energy ions bombardment. Simulations have also been carried out for different gap spacing between two electrodes and calculation results show that plasma density increases as the gap spacing decreases, as a result of lower electric field strength.

*Work supported by the National Science Council of ROC.

PS-TuP17 Numerical Investigation of Electron Heating in a Neutral-Loop Discharge Plasma, S. Kim, University of Wisconsin-Madison, S. Banna, Applied Materials Inc., Y. Nishi, Stanford University, J.L. Shohet, University of Wisconsin-Madison

Neutral Loop Discharge (NLD) plasmas are being investigated as a new plasma source to produce good directionality and high fluxes of ion bombardment at substrate surface¹ for semiconductor device fabrication. In an NLD plasma reactor, a Neutral Loop (NL) can be produced (zero-field path) that is generated by cusp-shaped magnetic field from direct current magnets. It has been shown theoretically that magnetic reconnection occurs in the neutral loop region when radio-frequency fields are applied². During the reconnection process, the DC magnetic field and the r.f. magnetic field cause disconnection and reconnection of the magnetic-field lines over an r.f. period. The reconnection results in the potential to heat electrons stochastically on the NL. Changing the position and the diameter of the NL can modify processing uniformity over a large area and thus improves plasma processing without need to move or rotate the workpiece. However, to confirm this, the details of plasma parameters as a function of position of the NL are produced by numerical simulations of electron motions near the NL in the presence of an r.f. The relationship between the r.f. magnetic field and its corresponding electric field and the average electron energy is also investigated.

This work was supported by the Semiconductor Research Corporation under Contact No. 2012-KJ-2359 and the National Science Foundation under Grant CBET-1066231.

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PS-TuP18 Hydrocarbon Conversion by Non-Equilibrium, Atmospheric-Pressure Microplasma, J. Cole, R.M. Sankaran, Case Western Reserve University

Hydrocarbon conversion plays an important role in our energy economy. For example, the conversion of natural resources such as methane into hydrogen, carbon monoxide, ethanol, and other chemical fuels is essential to current and future energy needs. Typically, hydrocarbon conversion (specifically, methane reforming) is carried out by high-temperature (>500 °C), catalytic processes. To lower the temperature requirements and improve the conversion and selectivity, non-equilibrium plasmas have been explored for the conversion of hydrocarbon feedstocks¹. However, the power requirements and stability at high pressures have been obstacles to achieving significant improvement. In this study, we explore the application of a novel class of atmospheric-pressure plasmas, microplasmas², for the conversion of hydrocarbon gases including CH₄ and CO₂. As carbon dioxide emissions increase globally, reactions consuming CO₂ may become a necessity. The reaction of CO₂ with CH₄, known as dry methane reforming, is endothermic and normally requires high temperature and pressure and a catalyst; however, a non-equilibrium microplasma could potentially carry it out at room conditions. Additionally, when coupled with a catalyst, plasmas in general have been shown to have a synergistic effect³ that improves conversion beyond that of just the plasma alone or catalyst alone.

In this study, CO₂ and CH₄ were introduced into a microplasma in varying feed ratios and flow rates. The effluent was characterized by simultaneous gas chromatography and mass spectrometry to identify and quantify

products. Reactive intermediate species were monitored by optical emission spectroscopy and soot formation was detected by aerosol ion mobility measurements. Results for CO₂ and CH₄ conversion as well as selectivity to specific products such as CO, H₂, and higher order hydrocarbons will be presented, as well as the formation of soot.

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PS-TuP19 Multi-Peaked and Stepped Electron Velocity Distributions in RF-DC Discharge with Secondary Emission, A. Khrabrov, I.D. Kaganovich, Princeton Plasma Physics Laboratory, P. Ventzek, L. Chen, Tokyo Electron America

Hybrid RF-DC capacitively coupled discharges find important and growing applications in industrial processes. In such discharges, secondary electrons emitted from the electrodes undergo a complicated motion defined by acceleration in, and bouncing between a steady and an oscillating sheath. For the secondary electrons that return to, and impinge upon the RF electrode, the arrival energy is a non-monotonic function of the driving voltage phase at which they were emitted. This basic property leads to a velocity distribution with multiple peaks [1,2]. This effect may explain the multiple peaks in the electron energy distribution function measured in RF-DC system at RF electrode [2,3]. The energy dependence upon the phase of arrival can also be discontinuous (as the number of bounces between the sheaths changes by plus or minus one), which corresponds to a distribution containing steps. Further, the velocity distribution of secondary electrons is sensitive to variations in the bouncing time and may form additional peaks if a small high-frequency ripple is present in the RF sheath voltage [2]. We have found such features in numerical test-particle simulations of the discharge, and analyzed the observed structure of the electron distributions. [1] D. Israel, K.-U. Riemann, and L.D. Tseng, *J. Appl. Phys.* **99**, 093303 (2006). [2] K.E. Orlov and A.S. Smirnov, *Plasma Sources Sci. Technol.* **10**, 541(2001). [3] L. Xu, L. Chen, M. Funk, A. Ranjan, M. Hummel, R. Bravenec, R. Sundararajan, D. J. Economou, and V. M. Donnelly, *Appl. Phys. Lett.* **93**, 261502 (2008).

PS-TuP20 Formation of Multi-Peak Electron Velocity Distribution Function by Two-Stream Instability in a dc Discharge, D. Sydorenko, University of Alberta, Canada, I.D. Kaganovich, A. Khrabrov, Princeton Plasma Physics Laboratory, L. Chen, P. Ventzek, Tokyo Electron America

Interaction of an electron beam with a plasma is of particular importance for hybrid dc-rf coupled plasma sources used in plasma processing. Electron acceleration by high-frequency waves may explain the low-energy peak in the electron energy distribution function measured in plasma processing devices [1]. In the present paper, the collisionless electron heating in a dc plasma source is studied using the particle-in-cell code EDIPIC [2,3]. In simulations, electrons emitted from the cathode surface are accelerated through a dc bias electric field and form an 800 eV electron beam entering the bulk plasma. The beam excites electron plasma waves via the two-stream instability. In the region of strong plasma oscillations bulk electrons can be accelerated to substantial energies. These energetic electrons are correlated with the peaks in the eedf described in [1]. In this presentation we discuss factors impacting peak energy and magnitude such as plasma profile. [1] L. Chen and M. Funk, *Langmuir wave standing wave resonance in DC/RF plasma*, Proceedings of ICRP 2010. [2] D. Sydorenko, A. Smolyakov, I. Kaganovich, and Y. Raitses, *Phys. Plasmas*, **14**, 013508 (2007). [3] D. Sydorenko, I. Kaganovich, Y. Raitses, and A. Smolyakov, *Phys. Rev. Lett.*, **103**, 145004 (2009).

PS-TuP21 Electron Molecule Collisions with Methane, W.J. Brigg, University College London, UK, A.I. Williams, S. Lopez-Lopez, D. Monahan, Quantemol Ltd., UK, J.C. Tennyson, University College London, UK, A. Dzarasova, Quantemol Ltd., UK

Methane is of particular interest due to its use in diamond deposition processes, and presence in fusion and combustion plasmas. Methane is known to be a difficult molecule to simulate, combined with the difficulty of obtaining electronic excitation and dissociation for both theorists and experimentalists alike[1], this presents a relative lack of data for this important molecule.

Quantum-mechanical calculations can be the answer. The calculations presented use the R-Matrix method: where the configuration space is divided into two regions. There is an inner region, where the physics is complicated by exchange and correlation effects, and an outer region, where

greatly simplified equations can be solved. The programs used to carry out these calculations are provided by the UKRmol suite. See Tennyson [2][3] for a detailed review of electron-molecule collisions using the R-matrix method. Quantemol-N provides an expert system for running these codes as well as adding extra functionality tailored to provide data for plasma models.

Using Quantemol-N, several different cross sections and properties were calculated for methane, including electron impact elastic, excitation, rotational excitation, differential, momentum transfer, ionisation, and dissociative attachment cross sections. This data can be covered in the reaction rates and used for modeling of plasma processes.

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PS-TuP22 A Comparative Study of New Algorithm for Fluid Simulation of High Density Plasma Discharges, S.G. Oh, Y.J. Lee, J.H. Jeon, J.H. Seo, H. Choe, Korea Aerospace University, Republic of Korea

The inductively coupled plasma or the capacitively coupled plasma reactors are typical ones in the material processes for the electronic device fabrications such as semiconductor, TFT-LCD, solar cell. Fluid simulation is one of the simulation method in transport modeling of these discharges, because the profiles of plasma quantities such as densities, temperatures, fluxes and potentials are easily obtained. It is known that there is a restriction on the simulation time step, because the shielding time scale of an electric field perturbation is very short. To overcome this limitation, semi-implicit methods are suggested for the solution of Poisson's equations. In this work, from the physical origin of restriction on simulation time step, a new method for larger time step in the steady-state fluid simulation of high density plasma discharge is suggested, and is explained. To study the differences and similarities, a simple comparison of the new method with previously known one is given.

PS-TuP23 Properties of a Magnetic Neutral-Loop Discharge, W. Li, S. Kim, K. Mavrakakis, Z. Ling, H. Zhang, J. Bray, T. Griffin, M. Nichols, University of Wisconsin-Madison, B.-H. Moon, Y.M. Sung, Kyungshung University, Korea, S. Banna, Applied Materials Inc., Y. Nishi, Stanford University, J.L. Shohet, University of Wisconsin-Madison

The magnetic neutral-loop discharge (NLD) was developed in 1994.[1] In this work we designed an NLD reactor using a stainless-steel chamber, instead of the commonly used quartz chambers in previous work because of the need for such a system in microelectronic processing. The vacuum chamber lies in the middle of three sets of magnet coils. With DC currents flowing in the opposite direction in the middle set of coils, a circle on which magnetic field is zero, *i.e.* a neutral loop(NL), can be produced in the middle of the chamber. In order to generate plasma, 13.56 MHz RF is inductively coupled into the chamber with a spiral antenna, through a quartz window located on one end of the chamber. The reactor can be operated in two modes, (1) an NLD mode when there are oppositely directed DC currents in the magnet coils, or (2) an ICP mode when there are either no DC currents or same direction DC currents in the magnet coils. In the NLD mode, the plasma was observed to be brighter near the location of the NL than in the center. This difference was further confirmed with measurement of the optical spectrum using an OceanOptics spectrometer, which shows the relative plasma glow brightness at the NL is as twice high as from the center of the chamber, and about 10% higher than the ICP plasma mode.

By adjusting the ratio of the DC currents running in the magnet coils, the radius of the NL can be changed. Both experiment and simulation show that the glow follows the change of the NL radius, especially at low pressure measured with a monochromator and photomultiplier and compared with that observed from the ICP mode as well as other reactors. Although the location of the argon peaks are the same, the relative heights of the peaks and their widths are strong functions of the operating pressure and r.f. power for both modes.

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PS-TuP24 Size Effect of Hf Liquidous Nano-particles on PEPVD Growth of HfSiON on SiO₂/Si, T. Haga, T. Kitajima, T. Nakano, National Defense Academy of Japan

In the paper, we show the size effect of metal particles on PEPVD of high-k dielectric thin film for MOSFETs.

In the case of a few deposition of Hf, high density hafnium metal nano particles with 2-6 nm diameter are formed on SiO₂/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with a SiN interface layer. The exposure of atomic nitrogen and ions from the non-equilibrium plasma enables the

introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS analysis. The nitridation rate is quite high and the quantitative measure shows the sticking of the N atom to the Hf nano particles reaches 1.0, while it is an order lower for thicker Hf layers more than 50 nm. A contact AFM survey of the Hf nano particles indicates the nano particles are liquidous due to Melting-point depression [2]. The following plasma exposure (~ 5 min.) enables the diffusion of Si atoms into the high -k film from the underlying SiO layer. Following N₂ ICP exposure continuously increases the N atom fraction in the film which is relatively slow compared to the initial stage. The XPS spectrum shows the sea incorporated is mostly nitrides in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

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PS-TuP26 High Etching Rate of Lithium Niobate Substrate using BCl₃/Ar Mixture Gases by ICP-RIE. C.M. Chang, P.L. Chen, J. Su, M.H. Shiao, C.-N. Hsiao, National Applied Research Laboratories, Taiwan, Republic of China

In this study, Z-cut LiNbO₃ single crystal wafers were etched by the inductively coupled plasma reactive ion etching (ICP-RIE) technique by using the boron trichloride (BCl₃)/ Argon (Ar) mixture gases. Effects of the ICP power and RF power ranged from 100W to 400W of the ICP-RIE system were studied on the etching rate, surface roughness, and corresponding DC bias under two working pressures of 30 mTorr and 50 mTorr, respectively. Besides, photoresist and metallic nickel thin film were used as the etching mask, and the selective ratios of the two etching masks were also compared. From the experimental results, it can be found that the DC bias (-V) decreases with the working pressure, and increases with the ICP power and the RF power. The surface roughness of the etched LiNbO₃ substrate was decreased from 55 nm to 30 nm with increasing working pressure, but it increased when the ICP power and RF power were increased. The etching rate of the LiNbO₃ substrate was increased with increasing the ICP power and RF power under the two working pressure. It is noted that the etching rate was greater than 100 nm/min when the working pressure was controlled at 30 mTorr. The selective ratios of the photoresist and the nickel were calculated to be approximately 0.4 and 8, respectively. Under suitable processing parameters of ICP-RIE, the surface roughness less than 40 nm, structure depth greater than 2 μm, and sidewall angle greater than 70° of the LiNbO₃ substrate can be obtained within 20 min, which etching rate is greater than 80 nm/min.

PS-TuP27 Direct Liquid Injection into Low-Pressure Plasmas. D. Ogawa, Chubu University, Japan, M.J. Goeckner, L.J. Overzet, The University of Texas at Dallas

What if a liquid is injected directly into low-pressure plasmas? The current material processing with low-pressure plasmas (< 100 Pa) requires the gas-phase precursors in many cases. The limitation is sometimes irritating. The technique we have proposed, *the direct liquid injection into low-pressure plasmas*, enables liquids for plasma processing without applying any heat. Also, this technique enables the injection of solids through a liquid. For example, one could control the number of nano-particles in a film that is produced with a plasma to change the mechanical property of the film. Or, one could leave the clusters of solids on a substrate by evaporating a liquid off to print a three-dimensional structure. It is also fine that one uses heat-sensitive materials such as proteins, or even bacteria because the temperature of plasma processing is generally low. This technique definitely expands the possibility of material processing with plasmas.

With our best knowledge, not so many people researched the combination of direct liquid injection and low-pressure plasmas. Coppins suggested these kinds of plasmas to call as *misty plasmas* [i] because one can consider that the droplets are another material state of particles. In contrast to dusty plasmas, misty plasmas can regulate the increase of particle temperature due to the droplet evaporation. Ward patented the configuration to realize the plasma processing in 2005. [ii] However, our experiences showed that the configuration should create unstable plasma so that the process should be difficult.

This presentation shows the some investigations of the technique from some theoretical calculations and from the experimental observations. Our calculations shows that the evaporation time of droplets becomes half even at a plasma with 10¹⁰ cm⁻³ and 2 eV due to the contribution of three-body recombination on the droplet surface. On the other hand, our experimental results are far from the computational results because of our technical difficulties. Our time-resolved measurements of plasma density and optical emission intensity showed that a plasma dimmed due to the massive vapor at the first several milliseconds. This means that the plasma gives almost no

contribution to the droplets' evaporation because the transport time of vapor is much shorter than that of droplets. This result indicates that the control of initial vapor plays a role to realize this technique. In the poster, we will summarize these results shown above with recent progresses.

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PS-TuP28 Role of Heterogeneous Surface Reactions on the Evolution of O and N Atoms in N₂/O₂ Flowing Afterglows. J. Pregent, L. Stafford, Université de Montréal, Canada

The number density of N and O atoms in the flowing afterglow of a reduced-pressure N₂/O₂ plasma sustained by propagating electromagnetic surface wave in the microwave regime was determined using a NO titration method. While the density of O atoms increased monotonously with increasing percentage of O₂ in the N₂/O₂ gas mixture, the N population first increased with trace amounts of O₂ and then decreased as the concentration of O₂ increased above ~0.1 %. Introduction of either Teflon, aluminum, stainless steel, or copper surfaces in the afterglow chamber influenced both N and O populations. The more prominent decrease was observed for Cu; a result consistent with the high heterogeneous recombination coefficient of O and N atoms on such surfaces. For all materials, the O-to-N number density ratio increased sharply with the addition of O₂, suggesting either a competition for surface recombination sites between N and O or the blocking of adsorption sites by physisorbed O₂. This latter mechanism affects more N than O recombination. A similar behavior was deduced from the analysis of the NO-B and N₂-B emission. Assuming that NO-B levels are populated by N+O+M->NO-B+M and N₂-B levels by N+N+M->N₂-B+M, where M is a third body, the NO-B/N₂-B emission intensity ratio becomes proportional to the O/N number density ratio. Over the range of experimental conditions investigated, we found that the ratio increased with the injection of O₂ in N₂. A less prominent increase was observed in presence of wood samples placed in the afterglow chamber, which indicates that O heterogeneous recombination reactions are more strongly affected by reactor walls or substrate properties.

PS-TuP29 Synthesis of Small Organic Molecules from a CO₂/CH₄ Mixture by Dielectric Barrier Discharge (DBD): Gas Composition and Power Effect. A. Ozkan, G. Arnoult, T. Bieber, P. De Keyser, F.A.B. Reniers, Université Libre de Bruxelles, Belgium

Carbon dioxide is usually considered as an end-product in chemistry because of its high stability. Due to the high quantities of CO₂ produced, its conversion received more and more attention in the recent years [1]. The transformation of CO₂, with CH₄ as second reactant and using atmospheric plasma technology shows that in good conditions, both gases can be converted into valuable products [2-3].

The conversion of CO₂/CH₄ mixtures was performed using a dielectric barrier discharge atmospheric plasma using Argon as the main plasmagen gas. Gas Chromatography was used to determine the composition of the gas after plasma treatment and this treatment was carried out in a new type of reactor developed in the laboratory. We demonstrated that the synthesis of syngas (CO and H₂) and small organic molecules such as C₂H₆, C₂H₄ is totally possible in this type of discharge [Fig. 1].

The study is focused on the effect of the plasma parameters on the CO₂ and CH₄ conversion rate. The parameters which are evaluated in this work are the ratio of CO₂/CH₄ flow rates and the power supplied.

We demonstrated that the CO₂/CH₄ ratio in the mixture has an important impact on the conversion rate. However, there is no real interaction between active species of these two gases since oxygenated organic compounds have only been detected at trace amounts. Nevertheless, the absence of oxygen after CO₂/CH₄ plasma is always obtained, suggesting that atomic oxygen is consumed in a plasma which contains only a few quantity of CH₄.

On the other hand, the effect of the power was clearly visible, showing a linear increase for both the CO₂/CH₄ conversion rates and the production of syngas according to the supplied power [Fig. 2]. This suggests that the number of electrons circulating between the electrodes has a huge impact on the conversion rate.

The detection of emitting species generated in the plasma (such as CO₂⁺ and CO₂ from the Fox, Duffendack and Barker's system, different peaks of H, OH, O...) was also carried out via optical emission spectroscopy (OES).

Finally, we observed a different effect of two plasmagen gases (Argon and Helium) on the conversion of CO₂ and CH₄. Indeed, the conversion of CH₄ is better when He is used as carrier gas compared to the use of Ar, whereas we observed an opposite effect for the conversion of CO₂.

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PS-TuP30 Mechanisms of Silicon Nitride (SiN) Etching by Hydrofluorocarbon (HFC) Plasmas, K. Miyake, T. Ito, M. Isobe, K. Karahashi, Osaka University, Japan, M. Fukasawa, K. Nagahata, T. Tatsumi, Sony Corporation, Japan, S. Hamaguchi, Osaka University, Japan

Selective etching of silicon nitride (SiN) over silicon dioxide (SiO₂) and/or silicon (Si) is widely used in the microelectronics industry. For example, the formation of dual stress liners or etching of dual/triple hard masks (DHM/THM) for dual-damascene structures requires highly selective SiN etching technology. It has been known that the use of plasmas based on hydrofluorocarbon (HFC) gases such as CHF₃ and CH₂F₂ or hydrogen (H) /fluorocarbon (FC) gases can result in higher etching rates of SiN. The goal of this study is to clarify the etching mechanism of SiN and SiO₂ by HFC/FC plasmas. For this purpose we have performed molecular dynamics (MD) simulations of SiN and SiO₂ etching by HFC/FC ions with improved interatomic potential functions. In the new interatomic potential functions, electronegativity of fluorine (F) bonded with carbon (C) is taken into account. It has been found that, in MD simulation, electronegativity of F strongly affects the etch rates of SiN by FC ions. Since F is highly electronegative and tends to attract electrons more strongly than C does, the CC bond of C-C-F or C=C-F is weaker than that of C-C-H or C=C-H and the C-F bond of C-C-F or C=C-F is stronger than that of CF₄. The bond energy of Si-F is comparable with that of the C-F bond. Therefore, when C and F atoms are provided from the incident beam to a SiN surface, the formation of C-F and Si-F bonds takes place simultaneously and the balance between the C-F and Si-F formation rates determines the total sputtering yield. Since SiF_x is a volatile species whereas CF_x radicals can form a polymer, if more SiF_x bonds are formed, etching proceeds more rapidly and, if more CF_x radicals are formed, polymer deposition takes place. In this study, we evaluate the sputtering yields of SiN by HFC/FC ions and examine the surface atomic compositions and desorbed products. The results are also compared with data obtained from ion beam experiments. Sputtering yields obtained from MD simulations with the new interatomic potential functions with more accurate electronegative effects of F are found to be in good agreement with those obtained from ion beam experiments.

PS-TuP31 Novel TSV Etching Technologies using Spatial and Temporal Control Plasma, Y. Morikawa, T. Murayama, T. Sakuishi, K. Suu, NMEMS and ULVAC, Inc., Japan

The advantage of high pressure ICP process is lower self bias voltage than capacitive coupled plasma (CCP) to reduction of notching profile for via last process. And, the very high frequency CCP can cause a plasma uniformity issue due to the standing-wave effect. The plasma characteristics of inductive coupled plasma (ICP) source above 10Pa process operated with dual rf antenna coils with magnetic neutral loop discharge (NLD) plasma were investigated for thru silicon via (TSV) etching. Improved plasma characteristics such as higher plasma density and very uniform and high aspect ratio anisotropy TSV etching process were realized in 300mm wafer. Which plasma source is kind of planar type ICP or NLD. 13.56MHz or 2MHz of rf for dual antenna coils and low frequency rf bias can operate independently. Mechanism of Si etching is mainly fluorine radical reaction. High density plasma is need to get high etch rate. On the other hand, management of radical diffusion from around rf antenna is important for very uniform process of high aspect ratio TSV as well. Center gas injection on the rf window is induced instead of side gas injection to avoid of the rf electric field effect. Therefore, when Si was etched using dual rf antenna coil with SF₆ / O₂ / SiF₄ or SiCl₄ mixture gases injection from center of rf window and outer side, the high etch rate and selectivity of Si over the photo-resist and very uniform process were observed. And, the combination of "spatial and temporal control of rf input power on dual rf antenna", and "gases inject apportionment each nozzles (center/outer)" can be controllable in large diameter substrate etching process. This method named "STEVIA" (Spatial and Temporal Control Plasma for Thru Silicon Via Etching).

PS-TuP32 State-Space Mapping of Plasma Tools via Coarse Mesh Tool Simulation, D. Monahan, Quantemol Ltd., UK, J.C. Tennyson, University College London, UK

The physical processes underlying low-pressure, low-temperature industrial plasma tools encompasses substantial ranges of space and time. This presents significant difficult for simulation. Large processing tools produce atomic scale features with process times often exceeding 1000's of seconds while applied frequencies are typically in the MHz or even GHz range. Tractable simulations, therefore, must typically make a number of rang limiting assumptions. An extreme simplification which is often employed when probing large parameters spaces is the "global-model" approximation, where volume-averaged chemistry balance equations are solved over the parameter space of interest. Though this may be regarded as an extreme approximation in view of the complexity of typical processing tool

geometries, careful consideration of the transport and loss effects often yields surprising agreement with experiment. However, these models do have limited potential and cannot hope to account for spatially dependent phenomena, which may play a significant role in many industrial processes. Spatially resolved simulations, on the tool level, are much less commonly employed for state-space exploration and are often restricted to limited regions of parameter space, or significantly simplified chemistries. However, as the prevalence of multi-core desktop computers continues to grow rapidly, it is not unusual for an engineer to have easy access to a great many processing cores. Utilizing relatively coarse mesh tool simulations, in conjunction with such computer resources now makes spatially resolved state-space mapping tool simulations feasible for short term investigations. In this poster we will present the results of such a study with an SF₆etching chemistry done using the new Quantemol - Virtual Tool (Q-VT) plasma simulation package.

PS-TuP33 Development of ICP Etching Processes for Gallium Nitride HEMT, S. Uehara, T. Nishimiya, Y. Kusuda, M. Hiramoto, S. Motoyama, O. Tsuji, SAMCO Inc., Japan

Next-generation power devices fabricated from wide band-gap semiconductors, such as Gallium Nitride (GaN) or Silicon Carbide (SiC), have the advantages of less energy consumption and smaller device size compared to Silicon power devices, and therefore, are expected to see application in hybrid and electric vehicles, trains, wind or solar power generators, and smart grid technology. This paper reports our recent development of manufacturing processes for a GaN High-Electron-Mobility Transistor (HEMT).

A planar structure GaN-HEMT enables high-speed switching with a two-dimensional electron gas (2DEG), but it is a normally-on device while a normally-off device is preferable. To realize normally-off planar GaN-HEMTs, precise thickness control of the AlGaN layer at the gate is necessary. However, reproducible, stable thickness control of the AlGaN layer in the etching process is challenging when manufacturing normally-off GaN HEMTs. For this reason, we developed a slow etching process with low damage and high reproducibility, combined with in-situ thickness measurement using an optical interferometric film thickness monitor.

Manufacturing GaN-HEMTs with a triple channel (Camel) structure requires an etching process with high GaN to AlGaN selectivity on the p-GaN substrate. We developed an etching process with GaN to AlGaN selectivity of 60:1. We also applied interferometric film thickness monitoring for high etch process reproducibility. Another challenge in the Camel GaN-HEMT structure is to prevent current collapse, which prevents drain current, caused by electron traps on the interface of the AlGaN and insulation layers. We managed this issue by lowering the interface states of the AlGaN.

PS-TuP34 Study of the Substrate Heating in a Magnetron Sputtering Process, J.S. Restrepo, University of Mexico, S. Muhl, J. Cruz, Universidad Nacional Autonoma de Mexico

The substrate heating by the plasma on the magnetron sputtering process is a knowledge process that has not been extended studied such as involve complex effects like ion, excited and neutral surface bombardment and radiation heat from the plasma. To this end we have constructed a multi-point thermocouple to study the spatial variation of the substrate heating under a range of experimental conditions, plasma power and Ar gas pressure during DC magnetron sputtering of titanium. Additionally, we have studied the effect of allowing the thermocouples to be floating, connected to ground and reactive environment. The results showed that the substrate temperature can reach temperature more than 200°C with a plasma power of 200W and that the highest temperature is localized in front at the race track due to a higher degree of particle bombardment.

Wednesday Morning, October 30, 2013

Electronic Materials and Processing
Room: 102 A - Session EM+PS-WeM

Oxides and Dielectrics for Novel Devices and Ultra-dense Memory II

Moderator: J. Kim, The University of Texas at Dallas

8:00am **EM+PS-WeM1 Active Surfaces and Interfaces in Valence Change Memory Type Oxides**, R. Waser, R. Dittman, RWTH Aachen University, C. Lenser, Forschungszentrum Juelich GmbH, Germany
INVITED

Flash memories and DRAM are ubiquitous today. However, a potential leap beyond the limits of Flash (with respect to write speed, write energies) and DRAM (with respect to scalability, retention times) emerges from nanoionic redox-based switching effects encountered in metal oxides (ReRAM). A range of systems exist in which ionic transport and redox reactions on the nanoscale provide the essential mechanisms for memristive switching. One class relies on mobile cations which are easily created by electrochemical oxidation of the corresponding electrode metal, transported in the insulating layer, and reduced at the inert counterelectrode (so-called electrochemical metallization memories, ECM). Another important class operates through the migration of anions, typically oxygen ions, towards the anode, and the reduction of the cation valences in the cation sublattice locally providing metallic or semiconducting phases (so-called valence change memories, VCM). The electrochemical nature of these memristive effects triggers a bipolar memory operation. In yet another class, the thermochemical effects dominate over the electrochemical effects in metal oxides (so-called thermochemical memories, TCM) which leads to a unipolar switching as known from the phase-change memories. In all systems, the defect structure turned out to be crucial for the switching process.

The presentation will cover fundamental principles in terms of microscopic processes, switching kinetics and retention times, and device reliability of the VCM-type ReRAM variant. It will describe what can be learnt about the nature of the redox-based switching process on open surfaces (e.g. system with top electrodes removed) and embedded electrode interface.

Despite exciting results obtained in recent years, several challenges have to be met before these physical effects can be turned into a reliable industrial technology.

8:40am **EM+PS-WeM3 Resistive Switching and Interface Structure of Metal / Ga₂O₃ / Metal Heterostructures**, B. Zhao, X. Zheng, H. Pham, M.A. Olmstead, F.S. Ohuchi, University of Washington

Materials exhibiting reversible resistance changes are essential elements of resistance random access memory (R-RAM), which has a simpler structure, lower energy consumption, higher operating speed and higher endurance than conventional RAM. The monoclinic transparent conducting oxide β -Ga₂O₃ is a promising candidate for R-RAM due to its open-channel structure that enables large scale defect migration. The resistive switching mechanism in pulsed-laser-deposited Ga₂O₃ was investigated by combining electrical measurements with x-ray diffraction (XRD) and sputter-profiling x-ray photoemission spectroscopy (SP-XPS), revealing a strong correlation of oxide-metal interface conductance with electrically and thermally driven defect migration and agglomeration near the interface.

Electrically-activated reversible resistance switching is observed in thin-film Ni/Ga₂O₃/Ir, while irreversible changes can be observed upon annealing either single-crystal or thin film gallium oxide. Room-temperature Ni deposition on single crystal β -Ga₂O₃ results in a rectifying contact with barrier height ~ 0.8 eV and SP-XPS reveals no interface reaction; annealing this structure to 500°C irreversibly creates an ohmic contact, as well as oxidized Ni and reduced Ga at the interface.

A reversible resistance change can be triggered by an electrical pulse in polycrystalline gallium oxide films grown by pulsed laser deposition. Ni/Ga₂O₃/Ir heterostructures were fabricated and then investigated at different points in their electrical cycling history. Application of less than about 10 V across a 100 nm film ($\sim 10^6$ V/cm) maintains the initial Schottky behavior; a 1 sec, 30 V electric pulse switches the metal/oxide contact from Schottky to Ohmic and increases the device conductance by two orders of magnitude. X-ray diffraction shows the film recrystallizes into α and β phases of Ga₂O₃; further electric field treatment increases the β -phase fraction. Sputter-profiling XPS shows an increase in the near-surface Ga:O ratio and introduction of reduced Ga within 2 nm of the metal-oxide interface. The film remains Ohmic under low voltage cycling, but a high-voltage pulse with the opposite polarity both reverses the interface chemical

changes and reverts the electrical characteristic to a Schottky contact. Further cycling between Ohmic and Schottky behavior continues with additional voltage pulses. The results are consistent with Ga interstitial migration and/or an interface redox reaction.

This project is supported by the National Science Foundation under DMR 1104628 and the Micron Foundation.

9:00am **EM+PS-WeM4 The Effect of High-Pressured N₂ Annealing in NiO_x based Resistive Random Access Memory**, D.H. Yoon, Y.J. Tak, J. Jung, S.J. Kim, H.J. Kim, Yonsei University, Republic of Korea

High pressure annealing (HPA) is known as an effective way to control the fundamentals of oxide system through the modification of stoichiometry, thermal decomposition, and compression.[1] Here, we report the effect of N₂ HPA on NiO_x based resistive random access memory (RRAM) device in terms of applied pressures in NiO_x system. In this research, the annealing temperature was fixed at 350 °C while the applied pressures were varied to 1, 20, and 50 atm. Pt was commonly used as bottom and top layer of metal-insulator-metal structure. As the N₂ pressure increased, the on- and off-resistance ratio was decreased from $\sim 10^5$ to $\sim 10^4$. However, the operation voltages (reset and set voltage) were reduced followed by increment of N₂ pressure. Specifically, the 50 atm HPA sample shows the lowest reset voltage of 0.95 V and set voltage of 2.12 V. This result implies that enhanced grain size was induced by the N₂ pressure as the grain boundaries are preference sites for conduction filament formation.[2] Furthermore, notable increment of non-lattice oxide component was confirmed which may cause the reduced driving voltages by x-ray photoelectron spectroscopy. These findings can enhance the understanding of low-power driving RRAM for next generation memory device.

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9:20am **EM+PS-WeM5 Ionic Memory - Materials and Devices**, M.N. Kozicki, Arizona State University
INVITED

There is widespread agreement within the semiconductor industry that existing high density non-volatile memory technologies are reaching their scaling limits and will ultimately be replaced by some variant of resistive random access memory (RRAM). This paper discusses advances in ionic RRAM, which relies on ion transport and redox reactions in thin solid electrolyte/dielectric films. Emphasis is placed on a technology known as Conductive Bridging Random Access Memory (CBRAM), a recently commercialized ionic memory based on the Programmable Metallization Cell (PMC) platform. In this technology, metallic cations are typically the mobile species. An ion current will flow if (1) the electrolyte is placed between two conductive layers, at least one of which can supply ions, (2) the ion-supplying electrode is made positive with respect to the opposing electrode, and (3) a sufficient bias is applied to overcome the internal potential barrier. The ion current feeds the reduction reaction, resulting in the formation of a metallic filament within the electrolyte/dielectric. The filament has a conductivity that is much higher than the surrounding material and hence it allows the resistance of the structure to be reduced by several orders of magnitude. The resistance of the conducting filament depends on the total number of metal ions that are reduced, which in turn depends on the charge supplied by the external circuit. Thus, the on-state resistance can be controlled by programming current and time. Control over the on-state resistance means that it is possible to create multiple discrete resistances levels to represent more than one binary digit per cell. If one electrode is electrochemically inert, the resistance-change process can be reversed by applying an opposite bias to that used for programming which dissolves the conducting pathway via oxidation of the metal in the filament. It is this electrode asymmetry that allows the deposition/dissolution process to be cycled repeatedly. We have also studied stackable diode-isolated arrays, in which each cell has one resistive switching element and one integrated Zener diode formed by the junction of the Cu filament of the device on-state and a doped silicon (n-type) electrode. The diode reduces "sneak path" currents via low resistance on-state devices in an array, but the reverse breakdown of the Zener element allows the cells to be erased by reverse bias.

10:40am **EM+PS-WeM9 Electrode-bias Injection and Percolation Controlled Transport through Vacated O-atom Site Defects in Nano-grain (ng-) TM Oxides and in Non-crystalline (nc-) Si(Ge)O₂**, *D. Zeller, G. Lucovsky*, North Carolina State University, *J. Kim*, University of Illinois at Urbana Champaign

Remote plasma CVD of thin film (i) non-crystalline nc-SiO₂ on Si substrates and (ii) nanograin ng-TM oxides thin-film dielectrics plasma processed Ge substrates combined removal of Ge-O and Ge-N layers by post-processing annealing presents new opportunities for devices.

Semiconductor conduction band edge states (CBES), and symmetries and singlet transport and/or trapping states of vacated O-atom defects are quantitatively different for nc-Si(Ge)O₂ and nano-grain (ng-) TM oxides. CBES in Si(Ge)O₂ and Si/Ge a zinc-blende III-V semiconductors are "s-like" with high electron mobilities. Combined with intrinsic band edge triplets in SiO₂, energies of vacated O-atom singlet defect states are deeper into the band-gap. Injection into, and transport through singlet defects localized in 1 nm nc-SiO₂ clusters with "crystalline-like" medium range order (MRO) extends to self-organized symmetric dihedral angles. Hopping transport through vacated O-atom sites is determined by percolation. It is eliminated through nc-Si(Ge)O₂ interfacial transition regions by the 0.6 eV spectral extent of the intrinsic band edge triplets explaining the absence of bulk negative space-charge in devices, and after accelerated bias-controlled stress testing. CBES and vacated O-defects in X-ray absorption spectra (XAS).

Properties of nc-SiO₂ dielectrics and their semiconductor interfaces are the standard against which high-k TM gate dielectrics are evaluated. CBES are "d-like" with symmetries dependent on coordination, "t_{2g}-like" for 6-fold coordinated TiO₂ and Ti₂O₃ and Magneli-phase alloys, and "e_g-like" for 7- and 8-fold coordinated HfO₂ and ZrO₂. Jahn-Teller effects remove 3-fold t_{2g} and 2-fold e_g degeneracy in O K-edge XAS in thin films <2 nm in TiO₂ and <3 nm-HfO₂.

In thicker films O-vacancy singlet states are below CBES with bias-controlled injection and transport. Combined with metal gates, and n- and p-type doping, for Si, Ge and III-V semiconductor substrates, memory and switching functionality is established. 300° CVD devices are obtained in RPD ~2 nm thick TiO₂ or HfO₂ onto nitrided Ge substrates with ~0.5 nm of Ge-N detected by in-line AES. 400-500°C post-deposition annealing removes Ge-N bonds at nitrided interfaces, and provides a template for deposition of nc- and ng-dielectrics. Ne-HfSiON on Si-passivated and nitrided Ge (100) and ng-TiO₂ yield Dit levels of 2-5x10¹⁰ cm⁻². C-V characteristics are symmetric with respect to flat-band voltages, V_{FB} yielding fixed charge levels ~2-3x10¹¹ cm⁻³. J-V characteristics yield currents at 1 V > V_{FB} of 3-5x10⁻⁶ A-cm⁻². TiO₂ capacitors on Ge have EOT values of ~4.5 nm, as well as low values of Dit.

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11:00am **EM+PS-WeM10 Investigation of the Dominant Conduction Mechanisms in Metal-Insulator-Metal Tunnel Diodes with Ta₂O₅ and Nb₂O₅ Dielectrics Deposited by Atomic Layer Deposition**, *N. Alimardani, J.F. Conley, Jr.*, Oregon State University

Thin film metal-insulator-metal (MIM) tunnel devices have seen renewed interest for high speed applications such as infrared (IR) detectors, optical rectennas for energy harvesting, and hot electron transistors. For many of these applications, desired properties include high asymmetry (η) and non-linearity (f_{NL}) of current vs. voltage (I-V) behavior and small turn-on voltage (V_{ON}). The standard approach to achieving these characteristics in tunnel devices is M₁IM₂ diodes - the use of electrodes with different workfunctions to induce a built-in field across the insulator. V_{ON} is influenced by the choice of the dielectric layer. In theory, small band-gap dielectrics with large electron affinity (χ) are desired to achieve small V_{ON} in tunnel diodes as they make small energy barriers with electrodes. Regarding this, Nb₂O₅ and Ta₂O₅ are widely considered to be promising candidates as tunnel dielectrics. In this work, we investigate Nb₂O₅ and Ta₂O₅ MIM diodes. Atomic layer deposition (ALD) was used to deposit 5 nm and 10 nm thick Nb₂O₅ and Ta₂O₅ tunnel barriers with sputtered amorphous bottom electrodes (ZrCuAlNi) and evaporated Al top electrodes. The I-V responses were found to be asymmetric for diodes made with 5 nm and 10 nm of either of these dielectrics. Although a lower V_{ON} was observed, the maximum asymmetry was 3 orders of magnitude smaller than what we previously reported for similar diodes with ALD Al₂O₃ as the

dielectric layer. High speed operation of MIM devices is typically based on Fowler-Nordheim tunneling (FNT). Conduction mechanisms were investigated as a function of temperature and electric field. By fitting I-V curves to FNT, Schottky emission (SE), and Frenkel-Poole (FP) emission plots, the dominant conduction mechanism in these diodes was found to be SE in the small bias regime (0.1 V to 0.3 V) and FP emission in the large bias regime (≥ 0.75 V). These assignments were confirmed by the close match of the optical dielectric constants extracted from the SE and FP plots with spectroscopic ellipsometry. Finally, Arrhenius plots show temperature dependence of current at both small and large bias regimes, indicating that tunneling is not the dominant conduction mechanism. In conclusion, we find that the small low-voltage asymmetric I-V behavior in MIM diodes made with Nb₂O₅ and Ta₂O₅ dielectrics is due to SE, rather than FN tunneling. A comparison will be made to bi-layer dielectric MIIM diodes, which we recently reported to show improved low voltage η and f_{NL} . This work indicates that the choice of dielectric is critical as high χ dielectrics may not exhibit conduction mechanisms appropriate for high speed applications of MIM tunnel diodes.

11:20am **EM+PS-WeM11 Mechanism of Light Emission and Optical Characteristics of Thin Film Metal Oxides**, *Y. Kuo, C.-C. Lin*, Texas A&M University

Currently, light emitting devices (LEDs) are made of inorganic or organic semiconductor materials prepared in crystalline thin films or nanocrystalline dots. They usually emit narrow band light due to the limit of the band gap energy of the semiconductor material. Commercial p-n junction or quantum well LEDs are fabricated with the MOCVD process involving toxic chemicals on the expensive single crystal substrate. Compared with the incandescent or the fluorescent light bulb, these LEDs have many advantages, such as the compact size, long lifetime, and low power consumption, but at the expense of the higher price, e.g., by more than one order of magnitude. On the other hand, the good-quality white light cannot be emitted from a single LED chip. It requires a set of three different LEDs or one LED in combination with a phosphor layer.

Recently, it has been reported that the broad band white light could be emitted from a new type of LED that has a MOS structure with a very thin amorphous metal oxide high-k dielectric layer (1,2,3). The complete device can be easily fabricated on the Si wafer using the IC compatible process at a low thermal budget. In this talk, authors will discuss 1) the light emission mechanism, which is from the thermal excitation of the conductive paths formed during the dielectric breakdown, 2) the optical characteristics, which covers the whole visible and part of the IR wavelength range of 400 nm to 1,000nm with a high color rendering index of 95, and 3) the lifetime, which is longer than 1,500 hours under the continuous operation at room temperature in the air. The unique physical structure and material properties of the sub 10 nm thick metal oxide layer are responsible for the light emitting phenomenon. Experimental results on this kind of device will be shown and discussed. In summary, this type of LED is applicable to a large range of industry, consumer, medical, etc. products.

(1) Y. Kuo and C.-C. Lin, *Appl. Phys. Lett.*, **102**, 031117 (2013).

(2) Y. Kuo and C.-C. Lin, *ECSSolid State Lett.*, **2(8)** Q59-Q61 (2013).

(3) Y. Kuo and C.-C. Lin, *Solid State Electronics*, accepted, August 2013.

Plasma Science and Technology

Room: 104 C - Session PS-WeM

Fundamentals of Plasma Surface Interactions

Moderator: S.A. Vitale, MIT Lincoln Laboratory

8:00am **PS-WeM1 Examination of Atomistic Etching Control of SiO₂-Si-SiO₂ Multi-Layers Stacks Using Cyclic Ar/C₄F₈ Plasma**, *D. Metzler, G.S. Oehrlein*, University of Maryland, College Park, *S.U. Engelmann, R.L. Bruce, E.A. Joseph*, IBM T.J. Watson Research Center

There is great interest in establishing directional etching methods capable of atomic scale resolution for fabrication of highly scaled electronic devices. We report on controlled etching of sub-nm thick layers of silicon and SiO₂ using cyclic Ar/C₄F₈ plasma. The work was performed in an inductively coupled plasma reactor. Use of SiO₂-Si-SiO₂ multi-layers on a Si substrate enables precise examination of selectivity, etch stop, and modification using *in situ* ellipsometry. Controlled etching is based on deposition of a thin (<1 nm) reactive fluorocarbon (FC) layer on SiO₂-Si-SiO₂ layers using pulsed C₄F₈ flow. Subsequent Ar⁺ ion bombardment removes the FC layer along with SiO₂ from the surface. Ar⁺ ion bombardment energies were selected so that once the FC layer had been removed, etching ceased. If ion energies are too high, significant SiO₂ etching takes place and a self-limited process cannot be achieved. The impact of deposited FC layer thickness on SiO₂

etching and etch selectivity relative to Si is examined and quantified. Additionally, x-ray photoemission spectroscopy (XPS) studies are used to investigate surface chemistry at various stages of the cyclic surface etching and will be reported. We found that chamber condition, especially inadvertent fluorocarbon deposition on the chamber walls concurrent with ultra-thin FC layer deposition on the substrate surface, can have a strong impact on the etch characteristics. The authors gratefully acknowledge financial support from National Science Foundation award CBET-1134273.

8:20am **PS-WeM2 Plasma Induced Surface Roughness of ArF Photoresist Examined by Plasma-Beam Processes**, *T. Takeuchi, Y. Zhang, K. Ishikawa, M. Sekine*, Nagoya University, Japan, *Y. Setsuhara*, Osaka University, Japan, *K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan

We report an observed relationship between chemical modifications and physical morphological roughness on a photoresist for ArF excimer laser photolithography in plasma beam irradiation. In fluorocarbon plasma, at the very beginning period, three stages of characteristics of chemical changes occurred upon surface roughening or wrinkling of the photoresist; (1) a rapid reduction of C=O bonds, (2) gradual formation of a fluorocarbon layer, and graphitic (sp²-C) or amorphous (sp³-C) carbon layer; (3) as elapsed incubation phase, i.e. lag, where reached a steady-state of chemical changes for fluorocarbon ion irradiation on the surface; finally morphological changes initiated. Those processes evolved within dose of $6 \times 10^{15} \text{ cm}^{-2}$ for ion energy of a few hundred eV [1].

Furthermore, in hydrogen plasma, especially in annealing at approximately 160°C, the photoresist surface was corrugated with size of the order of microns as similar as the report about mechanically buckling [2]. Subsequently the roughen surface was treated by the plasma beam irradiation, the roughness was developed with a size of the order of nanometers as same as the previous report [1]. Therefore we are revisiting the roughening process on the plasma process [3], and we will discuss on the roughening phenomena on the photoresist during plasma processes.

References [1] T. Takeuchi *et al.*, *J. Phys. D* **46**, 102001 (2013). [2] H. Jiang *et al.*, *PNAS* **104**, 15607 (2007). [3] R. Bruce *et al.* *J. Appl. Phys.* **107**, 084310 (2010).

8:40am **PS-WeM3 Sidewall Polymer Deposition for Achieving Near 1:1 x:y Critical Dimension Shrinkage**, *N.A. Fox-Lyon, D. Metzler, A.J. Knoll*, University of Maryland, College Park, *T. Liu, D. Farber*, Texas Instruments, *G.S. Oehrlein*, University of Maryland, College Park

New methods for shrinking lateral features are required to extend current generation photoresist patterning to smaller structures for devices. One approach for this is deposition onto sidewalls of patterned features using plasma-etch equipment. Current issues with this method are creating significant and uniform (x,y dimensions) pattern shrinkage and minimizing roughness and deformation of patterned features. In this work, we explored shrinking circular/elliptical holes and lines in 248 nm photoresist and 193 nm films using plasma-enhanced deposition in combination with etching. Both hydrocarbon and fluorocarbon plasma mixtures with inert/reactive carrier gases were evaluated for deposition. Plasma parameters for shrinkage were chemistry (e.g., ratio of deposition gas to carrier gas flow), pressure, applied power, ion energy (by substrate biasing), and deposition time. Real-time *in situ* ellipsometry and x-ray photoelectron spectroscopy of deposited films and scanning electron microscopy of patterns were carried out for characterization. We report on the plasma parametric dependencies of top-down and sidewall deposition rates, along with optical density and chemical composition of the films. Cyclical deposition/etching and pulsed plasmas were also explored for achieving shrink and minimizing sidewall roughness. Statistical analysis of x:y shrink, top-down deposition to sidewall deposition, and sidewall/surface roughening was investigated. We find strong dependencies on sidewall shrink on feature size and aspect ratios. As feature sizes get below 50 nm, minimizing feature roughness/occlusion becomes more difficult for the plasma parameters explored. Achieving significant 1:1 x:y sidewall shrink requires fine control of the plasma parameters that can change during deposition. By fine-tuning plasma parameters we have achieved 10's of nm of 1:1 x:y sidewall shrink of circular/elliptical patterned photoresist features.

9:00am **PS-WeM4 Plasma Energy Partitioning and Influences on Surface Reactivity**, *J.M. Blechle, M.F. Cuddy, E.R. Fisher*, Colorado State University

The partitioning of energy within plasma systems is of vital importance to plasma chemistry as it provides insight into reactivity via possible formation and decomposition mechanisms as well as its significant contribution to surface reactivity. Here, such investigations are used to determine the internal and kinetic energies of species within a variety of inductively coupled plasma systems. To obtain this information, optical emission spectroscopy (OES), broadband absorption spectroscopy (BAS),

and the imaging of radicals interacting with surfaces (IRIS) technique were utilized to determine species energetics (vibrational, rotational, and translational temperatures). Although comparisons will be made between internal energies of SiF in SiF₄ plasmas and CF in variety of fluorocarbon plasmas, a primary focus will be placed on nitric oxide plasma systems and the associated energies of NO gas species. These data are also correlated to species surface reactivity data, and are used to demonstrate the relationship between internal temperatures and observed surface scatter coefficients (S), which is directly related to surface reactivity (R). One such comparison will be on the strong correlations measured between the vibrational temperatures (Θ_v) of NO and S(NO) as a function of applied plasma power. Such observations allow for unique insight into these plasma systems and the integral role energy partitioning plays in the assessment and understanding of complex plasma chemistry.

9:20am **PS-WeM5 H₂/D₂/Ar Plasmas Interacting with Carbon-based Films: Plasma Distribution Functions, Etching and Applications**, *N.A. Fox-Lyon**, *A.J. Knoll*, University of Maryland, College Park, *J. Franek*, West Virginia University, *V. Demidov*, Wright-Patterson Air Force Base, *M. Koepke*, West Virginia University, *G.S. Oehrlein*, University of Maryland, College Park

Prediction and control of plasma distribution functions in low temperature plasmas are important for control of plasma-materials interactions. Reactive impurity additions to inert plasmas are important due to their large effects on both plasma properties and role in plasma-surface interactions. H₂ and/or D₂ added to Ar is an increasingly large topic of interest. The addition of small amounts of H₂/D₂ to Ar cause a change from physical to chemical sputtering of etching surfaces. Sode *et al.* have shown that small additions of H₂ to Ar cause unpredicted distributions of ion composition and a large loss in plasma density [1]. We investigate the effect that addition of small amounts of H₂/D₂ has on the ion compositions and energy distributions, along with effects on the plasma electrical properties and neutral and metastable species. D₂ addition to Ar plasma causes a faster transition to predominant ArD⁺ ions than H₂ addition causes transition to predominantly ArH⁺ ions. We also report on the effect H₂/D₂ added to Ar plasma has on the Ar metastable concentration. We find that, like the effect on plasma density, the metastable concentration decreases rapidly with the introduction of H₂ impurities. We find measurable differences for these effects when using D₂ impurity instead of H₂ impurity. The effect of these changes to plasma properties by H₂/D₂ impurity addition is also reflected in the plasma material interactions with hydrocarbon films. While ion mass falls gradually with addition, etch rate and modification change drastically. Direct plasma and neutral-based etching experiments were performed for different chemistries to separate the effects of ion composition/mass and reactive neutrals generated in the plasma. The authors gratefully acknowledge financial support from US Department of Energy (DE-SC0001939).

[1] Sode *et al.* *J. Appl. Phys.* **113**, 093304 (2013)

9:40am **PS-WeM6 Molecular Dynamics Simulation for Hydrogen Plasma Processing of Graphene**, *A. Davydova**, *E. Despiou-Pujol*, *G. Cunge*, Cnrs/ujf/ Cea - Ltm, France, *D.B. Graves*, University of California, Berkeley, *L. Magaud, L. Delfour*, CNRS/UJF, Institut Néel, France

Graphene is a two-dimensional material with unique physical, chemical and mechanical properties, promising for novel applications in industrial scale. The successful development of graphene-based thin film technologies relies on the capability to grow and integrate this material into sophisticated devices, but the nm-scale control of graphene processing challenges current technology, especially in plasma treatment.

The main issue associated with plasma/graphene processes is the few- to mono-atomic thickness of the material: graphene is easily damaged upon exposure to reactive plasma. This precludes the use of conventional plasma technologies to clean, dope and pattern graphene layers in a controlled way as is done for other materials in the microelectronic industry. Pulsed inductively coupled plasmas (ICPs) could in principle alleviate this issue by reducing ion bombardment energy while retaining active radicals. Hydrogen plasma has been shown to be promising for graphene treatment with minimal damage, but little is known of the fundamental mechanisms.

In this work, we applied classical molecular dynamics (MD) simulations of H₂ plasma / graphene interaction to assist the development of two important processes: graphene surface cleaning (selective removal of polymeric PMMA residues from its surface) and graphene nanoribbon (GNR) patterning with well controlled edges. Using MD we investigate the impact of the graphene temperature and incident H species energy on nanoribbon modification. We found that on the ribbon basal plane, H species experienced a repulsive force due to delocalized π-electrons, which prevents

* Coburn & Winters Student Award Finalist

them from chemisorption if their energy is below ~ 0.6 eV. By contrast, there is no barrier for H chemisorption on GNR edges and the graphene border can be rapidly hydrogenated by H radicals without damaging the basal plane. MD simulations further suggest that lateral etching will not occur unless the graphene temperature is raised above ~ 600 K and that etching probability slows above about 800K. This result is in good agreement with experiments. We also show that exposure of graphene to energetic H above a threshold of ~ 12 eV leads to H penetration through graphene. Severe damage of the graphene basal plane (i.e. C-C bond breaking) is observed at incident H energies higher than ~ 15 eV. This suggests that ions and fast neutrals from pulsed ICPs, which impact surfaces at $\sim 1-10$ eV, may be well suited for graphene cleaning and GNR trimming. This result has now been confirmed experimentally. XPS, AFM, Raman and electrical measurements show that pulsed H₂ plasmas clean PMMA residues from graphene surface with almost no damage after annealing.

10:40am **PS-WeM9 Beam Studies of Plasma Etching Reactions.** **K. Karahashi, S. Hamaguchi**, Osaka University, Japan **INVITED**

For the development of highly integrated semiconductor devices, more precise control of etching processes is required for further progress. For this purpose, it is desirable to have full understanding of surface reaction mechanisms associated with the etching processes. However, in general, it is difficult to analyze such reactions in detail for plasma etching processes because a large number of reactions take place simultaneously. One way to tackle this challenge is use a beam system to examine specific beam-surface interactions that are likely to take place in actual plasma etching processes. Pioneering work by Coburn *et al.* [1] using beam experiments clearly showed that silicon etching reactions on fluorinated surfaces are enhanced by energetic inert ion bombardment. Many such studies have provided useful qualitative information on silicon etching by plasmas based on, for example, halogen gases. As new advanced semiconductor devices have been proposed, the variety of materials that require highly controlled etching and that of gases that are used for the reactive ion etching (RIE) processes have increased significantly. Therefore we believe that needs for such beam studies are higher than ever. Based on an earlier beam system [2], we have recently advanced our techniques to examine interactions of reactive ions and free radicals with material surfaces, using a multi-beam system. With this system, we have obtained detailed information on reactive etching and physical sputtering processes on various materials such as silicon, silicon oxide, silicon nitride, and metals including ferromagnetic materials. The multi-beam system is a mass-selected ion beam injector combined with supersonic molecular beam and effusive molecular beam sources. When a sample is irradiated with any combination of these beams, it exhibits a specific surface reaction that would take place in an actual plasma. Its surface analyses include *in-situ* chemical analyses by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy and angular and time-resolved measurements of desorbing molecules by a rotatable QMS. In the presentation, a detailed account will be given of how such beam experiments unveil surface reaction mechanisms for RIE processes, based on examples of four recent studies on selective etching processes of Si-based materials and metals. [1] J. W. Coburn, H. F. Winters, and T. J. Chuang: *J. Appl. Phys.* **48**(1997) 3532. [2] K. Karahashi *et al.*: *J. Vac. Sci. Technol. A* **22**(2004) 1166

11:20am **PS-WeM11 Surface Cleaning for Enhanced Adhesion to Packaging Surfaces: Plasma and Free Radical Chemistries.** **S. Gaddam, H. Kasi, J. Kelber**, University of North Texas

In microelectronics device packaging, the removal of adventitious carbon and other contaminants, and the formation of a hydrophilic surface, are key steps to ensure adequate bonding to epoxy. This surface cleaning is commonly accomplished by oxygen plasma treatment, but the effects of such treatment on contaminant removal, surface composition and surface hydrophilicity are not well-understood. In-situ x-ray photoelectron spectroscopy (XPS) indicates that He, O₂ and NH₃ capacitively-coupled plasmas are equally effective at removing adventitious carbon from silicon nitride (SiN_x) and Si oxynitride (SiO_xN_y) surfaces. O₂ or He plasma treatment, however, results in initial oxidation of SiN_x or SiO_xN_y surfaces, and eventual formation of a SiO₂-like overlayer. In contrast, exposure of either surface to thermal atomic O yields carbon removal, but only surface oxidation of SiN_x, and no further change in SiO_xN_y surface composition. The data demonstrate that silica overlayer growth involves reaction of background O₂ or H₂O with reactive sites induced by ions or vacuum ultraviolet photons present in the plasma. In contrast, the exposure to NH₃ plasma results in negligible surface oxidation of the SiN_x or SiO_xN_y surface, but with effective removal of the adventitious carbon. There is no formation of a SiO₂ overlayer even at higher exposure times. This indicates that the presence of H passivates or reduces reactive sites for SiO₂ formation at the Si_xN_y or SiO_xN_y surfaces. Ex-situ contact angle measurements show that SiN_x and SiO_xN_y surfaces exposed to oxygen plasma are initially more hydrophilic than surfaces exposed to NH₃ plasma, indicating that the O₂

plasma-induced SiO₂ overlayer is highly reactive towards ambient. At longer ambient exposures ($> \sim 10$ hours), however, surfaces treated by either method exhibit similar steady state contact angles, correlated with rapid uptake of adventitious C, as determined by XPS. These data demonstrate that O₂ or even He plasma cleaning of SiN_x or SiO_xN_y surfaces results in unintended SiO₂ overlayer formation and that the use of NH₃ plasma can clean the substrates efficiently without the SiO₂ formation. The data also demonstrate that the hydrophilicity of such surfaces decreases rapidly upon ambient exposure, suggesting the potential advantage of *in-situ* surface passivation following plasma cleaning.

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Wednesday Afternoon, October 30, 2013

Plasma Science and Technology

Room: 104 C - Session PS-WeA

PSTD at AVS60: Looking Back and Moving Forward

Moderator: C.A. Wolden, Colorado School of Mines

2:00pm PS-WeA1 The Origins of the AVS Plasma Science and Technology Division, H.F. Dylla, American Institute of Physics INVITED

The AVS Plasma Science and Technology Division (PSTD), from its origins the mid 1980's through the present, has been a significant international forum for both the science and technology associated with the interaction of low temperature plasmas with materials. This talk will trace the origins of the PSTD from the formation of the Fusion Technology Division (FTD) in the late 1970's. The FTD's topical interests concerned both magnetic and inertial fusion devices that were undergoing rapid development at the time. Initial interests included the important plasma surface interactions that influenced the behavior of boundary plasmas and were used to condition the vacuum vessels of magnetic fusion devices or to prepare the multi-layer targets used in inertial fusion experiments. This concentration on plasma surface interactions laid the groundwork for broadening the FTD to the wider interests of the application of low temperature plasma for materials processing, and for rebranding the division to reflect its expanded focus.

2:40pm PS-WeA3 The Emergence of Plasma Processing, M.A. Lieberman, University of California, Berkeley INVITED

Plasma processing is a crucial technology for fabricating trillions of nanometer-size transistors on a silicon wafer [1]. It evolved from humble beginnings in the early 1900's: the silver-coating of mirrors by physical sputtering in dc glow discharges. The late 1950's - early 1960's saw extensive studies of physical and reactive sputtering in capacitive rf reactors. Isotropic plasma etching, mainly for photoresist stripping, was developed in the late 1960's - early 1970's, and etching of many other important materials was demonstrated. Three key advances in the late 1970's made plasma processing technology indispensable: (a) the discovery of ion-enhanced (anisotropic) etching [2]; (b) the development of SiO₂ etching with high SiO₂/Si selectivity [3]; and (c) the controlled etching of passivating films, e.g., Al₂O₃ over Al [4]. Etching discharges evolved from a first generation of "low density" reactors capacitively driven by a single source, to a second generation of "high density" reactors having two power sources, such as ICP's (rf inductive-driven) and ECR's (microwave-driven), in order to control independently the ion flux and ion bombarding energy to the substrate. A third generation of "moderate density" reactors, driven capacitively by multiple frequency sources, is now used, and there is increasing use of pulsed discharges to further control processing characteristics. The inductive reactors were invented 129 years ago [5], while the ECR's and the pulsed technology emerged in the aftermath of World War II [6]. Amazing challenges lie ahead as scale-down of transistor critical dimensions proceeds.

Supported by the Department of Energy Office of Fusion Energy Science Contract DE-SC0001939; special thanks to J.W. Coburn.

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4:00pm PS-WeA7 The Virtual World of Modeling Plasma Processing, M.J. Kushner, University of Michigan INVITED

Modeling of plasma processes has significantly advanced during the tenure of the AVS with benefits to investigating fundamental science issues and to technology development. Modeling's contributions to plasma processing science have been facilitated by a series of milestone contributions,

including development of accessible particle-in-cell simulations, use of molecular dynamics for investigation of surface processes, hybrid techniques which have expanded the variety of plasmas investigated, multi-phase models for dusty plasmas, technology relevant profile simulation, on-demand computation of cross sections, and now state-of-the-art algorithms embedded in commercially available modeling platforms. Although model development has been closely tied to applications, a collaborative development of fundamental theories has been exceedingly important to formulating proper and relevant technology focused models. The variety and dynamic range of plasma processing applications, from low pressure magnetrons to atmospheric pressure jets and now to liquids, has both challenged and benefited modeling. In other fields of applied physics, and other sub-fields of plasmas, the dynamic range of interest is markedly smaller and so resources have been concentrated on advancing modeling in more focused areas. Plasma processing, with its greater dynamic range, has been less focused with the unexpected benefit of finding more common ground between what appears to be quite different sub-fields of plasma processing. With this virtual capability, the plasma processing community has embraced computational experimentation as a necessary and beneficial tool. In this talk, a perspective will be provided of modeling's impact on science and technology development in plasma processing, and on future opportunities.

*Work supported by the Semiconductor Research Corp., DOE Office of Fusion Energy Science, National Science Foundation, Agilent Research Labs and HP Research Labs.

4:40pm PS-WeA9 Innovations in Diagnostics for Non-Thermal Plasma, N.St.J. Braithwaite, The Open University, UK INVITED

Internal electrical diagnostics of plasmas date back to the early days of plasma physics. The first innovation was the realisation that drawing currents between wires placed in a plasma does not measure conductivity - the current depends mainly on the non-neutral space charge sheaths around the wires. In 1926 Langmuir and Mott-Smith reported this in a systematic analysis. Langmuir and coworkers were then able to link the form of collected currents to the density of charged species and to the mean energy of the electrons. Their equipment was inexpensive and uncomplicated; their analysis was state of the art for the 1930s and could take up to an hour between measurement and quantitative result. Since then electrostatic (Langmuir) probes have been a standard tool for investigating low-temperature plasmas. The chief innovations in the Langmuir probe method have come from incremental improvements in the analysis of probe data and refinements of the method. Self-consistent analysis of particle collection, the inclusion of collisional factors and the Druyvesteyn method that yields electron energy distributions have now been truly popularized by the digital revolution, enabling sophisticated data acquisition and rapid processing: quantitative sub-ms plasma parameters in real time. Nevertheless, autonomous systems still have not mastered the insight of real experts. Less obvious, but equally important in opening up access to probe methods, was the development of vacuum compatible, ceramic epoxies. Many imaginative variations of electrostatic probes now deliver data on potentials, densities, energies and fluxes. These innovations were awaiting 'need' more than 'technology'. For instance, probes for plasma environments involving RF or electronegative gases were slow to evolve until the semiconductor manufacturing industry found both scenarios to be indispensable. The simplicity of Langmuir's probe is both an advantage (anyone can make one) and a disadvantage (the models for analysis are contentious and restrictive). A similar challenge has been faced by electromagnetic probes based on resonances and transmissions of microwave signals in and around low temperature plasmas with ns resolution, in real time. Microwave methods also owe a great deal to advances in materials and data acquisition, driven by the technological need for robust, minimally intrusive probing of plasmas as a dielectrics. Thus, C21, user-friendly, finite element methods have opened up microwave techniques for probing low pressure plasmas, long after fast oscilloscopes and programmable microwave sources had made them attractive options to the electrically minded plasma diagnostician.

5:20pm PS-WeA11 Plasma Surface Interactions and How They Limit Semiconductor Plasma Processing, R.A. Gottscho, K.J. Kanarik, S. Sriraman, Lam Research Corp INVITED

Semiconductor growth continues at a brisk pace, driven by consumer electronics. Meanwhile, the semiconductor industry is evolving and facing unprecedented technology and economic hurdles. Limits imposed by planar technology and a stalled lithographic roadmap threaten to slow down the rate at which density, cost, and speed improvements can be made. More intricate device designs hold the promise of extending Moore's Law, but they increasingly rely on high-precision plasma processes of deposition and

etching. This means that deposited films must be conformal and atomically smooth; and formation of the FinFET structure requires atomic-scale etch precision across not only the wafer but also from wafer to wafer and fab to fab. Precision process solutions are already known but making them cost-effective is difficult as they are prone to inefficiencies in plasma surface interactions. In this paper, we will review fundamental plasma surface interactions such as the kinetics and dynamics of transport, adsorption, and desorption. These interactions will be discussed in relation to the performance of processing equipment, and how the resulting limitations can be overcome with clever process solutions.

Advanced Surface Engineering Room: 203 C - Session SE+PS-WeA

Atmospheric Pressure Plasmas

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **SE+PS-WeA1 Tailoring Surfaces using Atmospheric Plasma Technologies : Examples, Challenges, Limits, Future, F.A.B. Reniers, Université Libre de Bruxelles, Belgium** **INVITED**

Atmospheric plasma present nowadays numerous applications in the treatment of surfaces. They can be used for the cleaning of metals, for the reduction of surface oxides, to increase the adhesion of polymers, to deposit a wide variety of coatings from anticorrosion ones to biocompatible ones, including hybrid multifunctional coatings. They also have an effect on the surface roughness. Although the principles of the main technologies used (dielectric barrier discharge, RF discharges,...) are well known, the mechanisms involved in the different processes are still partly to be determined. Through a few detailed examples, the talk will try to go deeper in the understanding of what is going on in the process. The current limitations of atmospheric plasma technologies (what can be done, and what cannot be done (yet)) will conclude the talk.

Some detailed examples :

- Understanding the mechanisms for etching PTFE by atmospheric plasma to make it superhydrophobic. Through a combined study of the gas phase and the polymer by optical emission spectrometry, dynamic water contact angle, AFM, XPS and weight measurements, we will evidence the selected effect of atomic oxygen, metastable helium and UV photons on the etching process. The etching study is extended to a range of other polymers, ranging from PE to PTFE, with an increasing number of fluorinated atoms. Different mechanisms are proposed.

- The deposition of atmospheric plasma coatings usually leads to coatings exhibiting a good adhesion to the substrate. This adhesion, evidenced by peeling test, can be studied at the molecular level. The case of poly-AMA coatings and Silane coatings on aluminum will be presented.

- Plasma polymerization is strongly influenced by the chemical reactivity of the precursor molecule. A wide selection of molecules of precursor molecules, liquid at room temperatures have been injected in dielectric barrier discharge (from pure C_xH_y , to C_xCl_y and C_xF_y , and esters such as nPIB, nPMA, AMA). We will show the effect of the double bonds on the final chemical structure of a coating, and on the deposition rate. We will also show that double bonds known to be unreactive in conventional polymerization can easily be activated in plasma. The effect of halogenated atoms present on the precursor is also studied

Finally, some perspectives regarding the future applications of atmospheric plasma will be discussed. Geometrical aspects, frequency range, hybrid coatings, microtexturing, deposition rates, will be approached.

2:40pm **SE+PS-WeA3 Defining Atmospheric Pressure Air Plasma Treatment Parameters for Bonding Sheet Molding Compound, L.P. Haack, A.M. Straccia, Ford Motor Company**

Sheet molding compound (SMC) is used in the automotive industry for constructing body closure panels, typically on vehicles of low volume where tooling costs can be kept to a minimum. SMC is a reinforced composite material consisting of dispersed strands of chopped glass fibers in a polyester/polystyrene blended resin along with surface additives and inorganic fillers. The SMC body panels are typically constructed with an inner structure and an outer skin that are mated by adhesive bonding. Epoxy adhesives are used to join the panels. Although the resin chemistry should allow for a strong covalent bond with the epoxy adhesive, instead poor bonding is often noted in production. This is mostly attributed to the use of internal and external mold release agents. Physical sanding will help improve bonding, but the process creates substantial amounts of dust and debris and is prone to human error. Atmospheric pressure air plasma is therefore being evaluated as an alternative to prepare the surfaces for bonding. Plasma was shown to improve bond reliability at low to moderate

levels of treatment. Interestingly, it also yielded impeccable bond durability at high to extremely high levels of treatment; conditions that would be deleterious to many plastics, especially polyolefins that can revert treatment at elevated temperatures. Measurements were conducted in an attempt to elucidate how this material interacts with the plasma to produce a surface exceedingly robust to bonding at an unexpectedly wide range of treatment conditions. Atomic force microscopy measurements gave insight into the amount of surface roughness created by the plasma treatments, while chemistry was determined by surface energy measurements and X-ray photoelectron spectroscopy (XPS). Dyne level testing was unable to accurately discern varying treatment levels since measurements reached 72 dynes/cm (the wetting point of water) even at lower treatment levels, while robust bonding occurred at still considerably higher dosage levels. Solvent wiping experiments along with XPS measurements revealed that, under the time constraints of the automotive manufacturing process, plasma treatments essentially achieve a condition of steady state that will remove material and yet still present a highly oxidized surface that is conducive to bonding. Thus, in practice, a condition of overtreatment is essentially unattainable.

3:00pm **SE+PS-WeA4 Correlation of Spectral Emissions of a He-O₂ RF Atmospheric Plasma Discharge with Polymer Surface Activation, V. Milosavljevic, M. Donegan, University College Dublin, Ireland, P.J. Cullen, Dublin Institute of Technology, Ireland, D.P. Dowling, University College Dublin, Ireland**

Atmospheric pressure non-thermal helium plasma jets are increasingly used in many processing applications due to their combination of inherent plasma stability and excellent reaction chemistry. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma jets maintain characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. From an application point of view, the activation of polymer surfaces can help to overcome the chemical inertness and low surface energy generally associated with these types of materials. Polymers, such as PET, are thermally damaged at relatively low temperatures and so a delicate balance must be reached where surface activation of the polymer is maximised, while thermal damage is prevented.

The atmospheric plasma system employed generates plasma using He-O₂ (in the range of 100-200 W), operates at a frequency of 27.12 MHz and uses a 5 cm wide beam applicator. The input variables on this system were: helium gas at a constant flow rate of 30 l/min, while secondary gas input: plasma power ratios are set by the manufacturer.

This work employs optical emission spectroscopy as a diagnostic technique for the measurement of atomic and molecular spectral emissions generated using the plasma jet system. The OES of neutral atomic spectral lines and molecular bands are investigated over a range of plasma process parameters. Wavelength resolve optical emission profiles suggest that the emission of helium's spectral lines shows that the high energy electrons have a larger influence than helium metastables on the overall spectral emission. Furthermore, the experimental data indicates that the use of high helium flow rates limits the significance of air impurities, e.g. N₂, for the creation and sustainability of plasma discharges in He-O₂ gas chemistry. The level of polymer surface activation was evaluated based on changes to the water contact angle of PET samples after plasma treatment. For the first time a direct correlation was obtained between polymer water contact angle changes and the OES measurement of the atomic hydrogen Balmer H α and molecular OH line emission intensities. Further work will be presented how the high helium flow rate is used in an attempt to minimize the ratio of gas convection to chemical reaction time scale (recombination). This is also favours the rapid transport of newly created radicals and excited species to the surface under treatment.

This work was a funded by SFI under the Precision cluster, the 'Fresh-Pack' project funded by the National Development Plan of Republic of Ireland and grant OI171006.

4:00pm **SE+PS-WeA7 Atmospheric Plasma Polymerization Enhanced by Simultaneous UV Irradiation, N. Vandecasteele, J. Bossert, Université Libre de Bruxelles, Belgium, A. Kakaroglou, Vrije Universiteit Brussel, Belgium, B. Nisol, Université Libre de Bruxelles, Belgium, H.A. Terry, Vrije Universiteit Brussel, Belgium, F.A.B. Reniers, Université Libre de Bruxelles, Belgium**

Plasma polymerization is now commonly used to deposit a wide variety of films for various applications (corrosion protection, biocompatibility, ultrahydrophobic layers...). Atmospheric plasma polymerization is a very promising technique for thin film deposition in industry. Indeed it does not require the use of organic solvent and it is not limited by vacuum requirement. Furthermore the high reactivity of the plasma medium allows for a rapid deposition of a large number of molecules on virtually any kind of substrate.

However there are still some issues remaining: the degree of crosslinking is not always sufficient to ensure good barrier and mechanical properties of the films. In some instances the adhesion of the films to the substrate is not strong enough. In this study we looked at the plasma polymerization of Allyl methacrylate on gold substrate using a high frequency (17 kHz) dielectric barrier discharge (DBD). The effects of the classical plasma polymerization parameters (monomer concentration, power, deposition time...) are studied as well as the effect of in situ ultra violet (UV) irradiation. The UV source is a mercury discharge lamp commonly used to cure polymers. Our experimental setup consists of a 2 mm thick quartz plate (acting as the dielectric) covered with a stainless steel grid (diameter 0.018 mm, spacing 0.045 mm) acting as the powered electrode. The second electrode is made of a grounded copper plate. It is separated from the powered electrode by a 3mm gap. The UV lamp is placed directly above the quartz electrode, illuminating the sample through the grid. Argon is used as the plasma gas. Its flow ranges from 1 to 3 liter per minute (LPM). The precursor vapor is carried in the plasma by a secondary argon line with flow ranging from 1 to 3 LPM. The total gas flow is kept constant at 4 LPM.

Three separate cases are studied: plasma polymerized films (pp-film) without UV irradiation, pp-films with post plasma UV irradiation and finally pp-films with UV irradiation during the plasma polymerization.

The pp-films are characterized by FTIR, XPS, contact angle and ellipsometry. Differences between the pp-film compositions have been evidenced for the 3 types of treatments. Increased O/C ratios have been observed for the films exposed to UV irradiation. The FTIR spectra are also strongly affected by the presence of UV irradiation. Changes in the C=O/C-C peaks ratio are observed for the 3 types of treatments. This allows us to conclude that the irradiation during the films growth leads to different results than the usual UV post treatment (UV curing).

4:20pm SE+PS-WeA8 Plasma Polymerization of (3-aminopropyl) Trimethoxysilane using a Micro-plasma Printing Setup, J.R.G. Schalken, Eindhoven University of Technology; InnoPhysics B.V., Netherlands, *A.A.E. Stevens, P. Verhoeven,* InnoPhysics B.V., Netherlands, *M. Creatore,* Eindhoven University of Technology, Netherlands

Amino-functionalities are introduced in biosensors in order to specifically bind proteins using biomolecules for the detection of diseases from human blood samples. Plasma polymerization of amine-containing precursor molecules such as (3-aminopropyl) trimethoxysilane (APTMS) can be used to deposit films with amino-functionalities.

The μ PlasmaPrint technique utilizes a pin-to-plate dielectric barrier discharge at atmospheric pressure. A dielectric substrate is placed on a high-voltage plate electrode. An array of needles is moved above the substrate, while individual needles are allowed to move towards the surface and back based on a digital pattern. According to the Paschen law, a reduction of the distance between a grounded needle electrode and the high-voltage substrate holder from about 800 μ m to 200 μ m can lead to the ignition of a plasma. Within a millisecond the plasma is turned off by moving the needles up again. The dot-wise exposure of the surface to short micro-plasmas enables a local plasma treatment with a minimum feature size of 100 μ m.

Thin films of plasma polymerized APTMS have been deposited on a fluorinated ethylene propylene copolymer (FEP) using the μ PlasmaPrint technique. The thickness of the deposited films varied in the range of 5 to 100 nm. The surface characteristics and ageing behavior of the films have been investigated by X-ray photoelectron spectroscopy (XPS), fluorescence microscopy and water contact angle measurements, respectively. Depending on the number of print repeats of the μ PlasmaPrint system, the concentration of amino-functionalities in the deposited film as derived from XPS peak analysis varied from 9.1% for a single print repeat, down to 4.7% for 20 print repeats.

Water contact angle measurements showed an increase from 10° for a single print repeat up to 40° for 20 print treatments, while the water contact angle of the FEP substrate was measured to be 110°. The increase in water contact angle with increasing print repeats suggested a reduction of polar components at the surface and was therefore consistent with the relative reduction of amino-functionalities as measured with XPS.

Based on the experimental results, a polymerization process of APTMS is proposed. It is suggested that polymerization mainly takes place by the abstraction of methyl- and methoxy- groups to develop siloxane chains. For an increased number of print repeats, which results in a prolonged plasma exposure, it is proposed that the creation of reactive sites for the cross-linking of APTMS polymer chains also takes place in the aminopropyl chains, resulting in a decreased concentration of amino-functionalities.

4:40pm SE+PS-WeA9 Evaporative Coating at Atmospheric Pressure (ECAP), Y.L. Wu, J. Hong, D. Peterson, J. Zhou, T.S. Cho, D.N. Ruzic, University of Illinois at Urbana Champaign

Recently, the Center for Plasma-Material Interaction (CPMI) has developed innovative coating method of Evaporative Coating at Atmospheric Pressure (ECAP). This new idea is an atmospheric pressure based process following the similar concept as the Laser Pressure LAPCAP purely at Atmospheric Pressure (LAPCAP) [1], the material captured by the plasma plume is atomic in nature (the evaporated metal atom) and should therefore end up deposited molecule-by-molecule in a PVD fashion. By using the thermal energy from the microwave plasma solid 99.99%+ purity aluminum are evaporated and then produce a PVD-like alumina coating on a workpiece. The Aluminum target is inserted in the center of the microwave torch feeding a melt pool and evaporates into the surrounding plasma plume. A bottle neck was made in the antenna and could reduce the heat loss by 84%. The film was deposited as Al₂O₃ using oxygen from the environment. Alpha and other metastable phases of aluminum oxide were found on the deposited films. Deposition rate was around 2 μ m/min. Gas flow rate around the antenna tip was about 0.9 m/s, and temperature of the plasma was about 1400°C at 1350W input power from simulations. Gas shield was used to keep the work gas pure. A much higher thermal energy of the plasma plume will make a superior coating microstructure as compared to a purely evaporated film.

Reference:

[1] Laser-assisted plasma coating at atmospheric pressure: production of yttria-stabilized zirconia thermal barriers, Zihao Ouyang *et al* 2011 *J. Phys. D: Appl. Phys.* 44 265202

5:00pm SE+PS-WeA10 Selection of an Atmospheric Plasma Source for 450mm Backside Wafer Cleaning, F.T. Molkenboer, J. Van Veldhoven, Y.L.M. Creyghton, O. Kievit, T.W. Versloot, N.B. Koster, TNO Technical Sciences, Netherlands

TNO is working on the selection and development of a non-thermal atmospheric plasma source for backside wafer cleaning. This selection started with a theoretical comparison of the potential candidates. Main criteria for the selection are cleaning speed, the amount of contamination that can be removed in a certain time and plasma temperature. Further criteria are the dependency of plasma homogeneity on substrate conductivity, the distance between the plasma source and the substrate as well as scalability of the source up to a 450 mm wide cleaner. Backside wafer cleaning is important for the semiconductor industry to enable the transition from 300 mm wafers to 450 mm wafers. Contamination on the backside of a wafer can lead to printing errors and can negatively influence post lithography processing like metal deposition.

The selection of the plasma source is part of a TNO project that has the objective to build and deliver a complete backside wafer cleaner to the 450 mm pilot line to be installed at IMEC, Belgium. The final selection will be made on the basis of a series of experiments. Candidates already tested are surface- and volume- dielectric barrier discharge (SDBD and VDBD) plasma sources.

In this presentation we will report the outcome of our selection of the plasma source, supported by the validated source inventory and experimental results.

This work is funded by the ENIAC Joint Undertaking and AgentschapNL. It has the goal to enable the European semiconductor industry to make the transition to 450mm wafers

5:40pm SE+PS-WeA12 Rapid Atmospheric Pressure Plasma Jet Treatment on ZnO for rf-sputtered MgZnO/ZnO Heterostructures, S.T. Lien, H.C. Li, Y.J. Yang, C.C. Hsu, I.C. Cheng, J.Z. Chen, National Taiwan University, Taiwan, Republic of China

MgZnO/ZnO heterostructures have shown great potential for optoelectronic device applications. The polarization field at MgZnO/ZnO heterojunction can induce charge accumulation at the interface to form two-dimensional electron gases (2DEGs). This has been observed in high quality materials grown by molecule beam epitaxy (MBE) or pulse laser deposition (PLD) as well as in defective MgZnO/ZnO heterostructure system deposited by rf-sputtering. Although high quality MgZnO/ZnO is desirable for its high electron mobility, the required deposition technique such as MBE or PLD is not suitable for the processing of large-area electronics. In regard to large-area deposition, rf-sputtering technique is the preferred process in spite of the more defective nature of the deposited materials. In our previous studies, we have demonstrated that the electron Hall mobility of ~40 cm²V⁻¹s⁻¹ and field-effect mobility of ~84 cm²V⁻¹s⁻¹ in the rf-sputtered Mg_{0.4}Zn_{0.6}O/ZnO heterostructure and the top-gated Mg_{0.2}Zn_{0.8}O/ZnO thin film transistor, respectively. The mobility exceeds the typical value (6 to 9 cm²V⁻¹s⁻¹) of a-InGaZnO TFT, which is the most promising technique for large-area oxide electronics nowadays.

One key step to obtain 2DEGs in the *defective rf-sputtered* MgZnO/ZnO heterostructures is the thermal annealing process on ZnO prior to the deposition of MgZnO material. This paper reports that atmospheric pressure plasma jet (APPJ) treatment can be used for the same purpose with a much shorter processing time. A thirty-second APPJ anneal on ZnO with a maximum temperature of 340 °C can replace a 30 min, 400 °C furnace-anneal to promote the formation of 2DEGs in the rf-sputtered MgZnO/ZnO heterostructure. The APPJ treatment also increases the crystallinity of ZnO films and releases the compressive residual stresses, verified by XRD and UV-Vis transmission measurements. The ultra-short processing time is attributed to the synergy of plasma reactivity and temperature of APPJ.

Thursday Morning, October 31, 2013

Spectroscopic Ellipsometry Focus Topic

Room: 101 A - Session EL+AS+EN+PS+SS+TF-ThM

Spectroscopic Ellipsometry for Photovoltaics and Instrument Development

Moderator: M. Creatore, Eindhoven University of Technology, Netherlands

8:00am EL+AS+EN+PS+SS+TF-ThM1 Application of Spectroscopic Ellipsometry for the Characterization of Various Solar Cell Devices, *H. Fujiwara*, Gifu University, Japan **INVITED**

To establish new structural characterization methods for Si-based and CuInGaSe₂(CIGS)-based solar cells, we have developed spectroscopic ellipsometry (SE) techniques that can be applied for the analysis of various textured structures used in the solar cell devices. In particular, our SE analyses allow the structural characterization of (i) hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ -Si:H) tandem-type solar cells, and (ii) a-Si:H/crystalline Si (c-Si) heterojunction solar cells, both fabricated on textured substrates. For the determination of a-Si:H and μ -Si:H properties, optical databases in which the optical constants of a-Si:H and μ -Si:H are described by micro-structural factors have been constructed.^{1,2} Furthermore, by developing a new optical model, we have confirmed that the high-precision analysis of a-Si:H/ μ -Si:H multilayer stacks can be performed even on textured substrates having sub-micron size rough surface. On the other hand, to determine the thickness and properties of a-Si:H layers incorporated into textured a-Si:H/c-Si solar cells, SE with a tilt angle measurement configuration^{3,4} has been employed. In this technique, samples are tilted so that the specular light reflection on the texture facets is measured. From this technique, we have succeeded in characterizing the properties of quite thin a-Si:H layers (5 nm) on the c-Si textures. Recently, we have applied the SE technique further to establish the structural characterization method for CIGS-based solar cells.⁵ For the SE analysis, we have constructed an optical database in which the CIGS dielectric function can be calculated as functions of the Ga composition $x = \text{Ga}/(\text{In} + \text{Ga})$ and Cu composition $y = \text{Cu}/(\text{In} + \text{Ga})$. By using the constructed optical database, we have demonstrated that the structure and compositions of CIGS-based thin films can be determined accurately.

1) Kageyama et al., Phys. Rev. B 83, 195205 (2011), 2) Yuguchi et al., J. Appl. Phys. 111, 083509 (2012), 3) Saenger et al., Thin Solid Films 518, 1830 (2010), 4) Watanabe et al., Appl. Phys. Express 3, 116604 (2010), 5) Minoura et al. J. Appl. Phys. 113, 063505 (2013).

9:00am EL+AS+EN+PS+SS+TF-ThM4 Real-Time and Through-the-Glass Mapping Spectroscopic Ellipsometry for Analysis of CdS/CdTe Coated Superstrates and Correlations with Solar Cell Performance, *P. Koirala, J. Chen, X. Tan, R.W. Collins*, The University of Toledo

In-situ real-time spectroscopic ellipsometry (RT-SE) from the film side has been applied along with ex-situ spectroscopic ellipsometry through the glass (TG-SE) toward the analysis of the different stages of CdS/CdTe solar cell fabrication in the superstrate configuration. The RT-SE studies of the CdS and CdTe layers deposited on transparent conducting oxide (TCO) coated glass superstrates provide information on the CdS growth, its surface roughness evolution, as well as overlying CdTe interface formation and bulk layer growth. Such information is very useful for developing a realistic optical model for the as-deposited layer structure in TG-SE mapping analysis over the full 15 cm x 15 cm superstrate area. In the mapping analysis, a mask is used to measure all 256 points where 0.125 cm² area dot cells are to be made. Because the as-deposited superstrate/film-structure undergoes additional processing steps, however, in order to complete the solar cell devices, three sets of TG-SE data maps are collected that characterize the superstrate/film-structure in the (i) as-deposited, (ii) CdCl₂-treated, and (iii) back-contact patterned states. With the optical database that has been established for both the as-deposited and CdCl₂ treated CdS and CdTe, each of the three TG-SE data maps has been analyzed based on an optical model deduced from RT-SE studies of the CdS and CdTe depositions. By using these SE techniques, we have been able to quantify the spatial dependence of the changes that occur in the superstrate/film-structure as a result of the different processing steps. In order to corroborate the layer structure determined by TG-SE, comparisons with cross-sectional transmission electron microscopy (XTEM) have been performed for selected states of the superstrate/film-structure and for selected locations. The results have been found to validate the overall RT-SE and TG-SE approach and analysis results. Finally, the layer parameters as determined from the TG-SE analyses have been correlated statistically with the device performance of the 256 dot cells fabricated over the final 15 cm x 15 cm

superstrate/film-structure. The resulting correlations expedite solar cell optimization.

9:20am EL+AS+EN+PS+SS+TF-ThM5 Expanded Beam Spectroscopic Ellipsometry for In-line Monitoring of Thin Film Process, *M. Fried*, Hungarian Academy of Science, Hungary **INVITED**

Non-destructive analysing tools are needed at all stages of thin film process-development, especially photovoltaic (PV) development, and on production lines. In the case of thin films, layer thicknesses, micro-structure, composition, layer optical properties, and their uniformity are important parameters. An important focus is to express the dielectric functions of each component material in terms of a handful of wavelength independent parameters whose variation can cover all process variants of that material. With the resulting database, spectroscopic ellipsometry coupled with multilayer analysis can be developed for on-line point-by-point mapping and on-line line-by-line imaging.

This talk will try to review the investigations of different types of PV-layers (anti-reflective coating, transparent-conductive oxide (TCO), multi-diode-structure, absorber and window layers, backreflector) showing the existing dielectric function databases for the thin film components of CdTe, CIGS, thin Si, and TCO layers.

Off-line point-by-point mapping can be effective for characterization of non-uniformities in full scale PV panels in developing labs but it is slow in the on-line mode when only 15 points can be obtained (within 1 min) as a 120 cm long panel moves by the mapping station. Last years [1, 2], a new instrumentation was developed that provides a line image of spectroscopic ellipsometry (wl=350-1000 nm) data. Upto now a single 30 point line image can be collected in 10 s over a 15 cm width of PV material [3, 4]. This year we are building a 30 and a 60 cm width expanded beam ellipsometer which speed will be increased by 10 X. Then 1800 points could be mapped in a 1 min traverse of a 60*120 cm PV panel or flexible roll-to-roll substrate. Another enhancement is the switch-over to rotating compensator measuring principle.

[This work was supported by the ENIAC E450EDL and KMR_12_1_2012_0225 projects]

[1] C. Major, G. Juhasz, Z. Horvath, O. Polgar, M. Fried, *PSS (c)*, **5**, 5 (2008).

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[3] M. Fried, G. Juhász, C. Major, P. Petrik, O. Polgár, Z. Horváth, A. Nutsch, *Thin Solid Films***519**, 2730 (2011).

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10:40am EL+AS+EN+PS+SS+TF-ThM9 Materials Characterization using THz Ellipsometry and THz Optical Hall Effect, *T. Hofmann*, University of Nebraska-Lincoln **INVITED**

Ellipsometry in the THz spectral range has been demonstrated to be a very versatile tool for the investigation of semiconductor heterostructures, meta-materials, 2D electron gases (2DEG), and even graphene.

In this talk, instrument development with particular emphasis on frequency-domain, rotating optical element THz ellipsometry will be reviewed and recent progress on THz optical Hall-effect systems, which encompasses generalized ellipsometry in magnetic fields, will be discussed.

The application of THz ellipsometry for the accurate measurement of complex optical constants of isotropic and anisotropic bulk materials and thin films will be illustrated briefly. The progress on THz generalized ellipsometry investigations of 3D metal nanostructured thin films will be reported in detail. The investigated films exhibit a strong anisotropic optical response in the THz spectral range. It will be demonstrated that the anisotropic optical response of 3D nanostructures changes drastically as the function of the dielectric properties of the ambient. Applications for 3D metal nanostructured thin films as THz optical sensors will be discussed.

In addition, recent results on application of THz optical Hall-effect measurements will be reported. Exemplarily, temperature-dependent THz optical Hall-effect investigations of AlGaIn/GaN high electron mobility transistors structures are shown. Our findings indicate that the 2DEG sheet density is independent of the sample temperature. The mobility and effective mass, however, strongly depend on the sample temperature. The mobility shows a strong increase with decreasing temperature largely due to the reduction of LO phonon scattering. The opposite behavior is observed for the effective mass and explained by the reduction of the 2DEG

confinement, i.e., the wave function penetration of the AlGaN with increasing temperature.

11:20am **EL+AS+EN+PS+SS+TF-ThM11 A History of Early Ellipsometry and Polarimetry, R.A. Synowicki, J.A. Woollam Co., Inc.**
This work surveys the early history of polarimetry and ellipsometry. Special consideration is given to the time period between Drude's original work in the late 1880's and the work of Rothen in the mid 1940's.

Snell determined the refractive index of water in 1621. Isaac Newton followed in the 1660's with the prism minimum deviation technique. In the late 1880's August Kundt measured the optical properties of very thin metal films by minimum deviation, but a better technique was needed for absorbing materials.

The polarimeter was invented around 1840. Early polarimetry was used to measure the rotation of polarized light through solutions of sugar, and used in customs offices at seaports for taxation of sugar shipments. In 1845 the Faraday effect showed rotation of polarization by a magnetic field, a result later explained by James Clerk Maxwell's electromagnetic theory.

Paul Drude applied Maxwell's theory to describe the internal structure of materials. To experimentally determine optical properties Drude developed ellipsometry as an analytical technique between 1885 and 1890. Null ellipsometry techniques were originally used, but in the following decades half-shade techniques with improved accuracy became common.

Ellipsometry remained a popular technique after the time of Drude. A surprising amount of this early ellipsometry work was spectroscopic. By 1910 R.S. Minor, A.Q. Tool, and L.R. Ingersoll used ellipsometry to determine the optical constants of metals over a wide spectral range from 226 nm in the ultraviolet to 2250 nm in the infrared.

11:40am **EL+AS+EN+PS+SS+TF-ThM12 Vibrational Properties of Lanthanum Aluminate and Magnesium Aluminate Spinel Using Fourier Transform Infrared Ellipsometry, T. Willett-Gies, New Mexico State University, C.J. Zollner, Cornell University, E. DeLong, S. Zollner, New Mexico State University**

Using FTIR ellipsometry, we have determined the dielectric function of twinned single-crystalline lanthanum aluminate (LaAlO_3) and spinel (MgAl_2O_4) wafers which are often used as substrate materials for oxide epitaxy. Measurements were taken at 300 K in the region of lattice vibrations between 250 and 1000 cm^{-1} . LaAlO_3 is a rhombohedrally distorted perovskite with two formula units per unit cell, leading to eight IR-active phonon modes [1]. Two of these eight are below our spectral range, one is very weak, and two are nearly degenerate [1]. We thus expect four TO peaks in the imaginary part of the dielectric function. The polar character of LaAlO_3 also causes strong LO-TO splittings. Unlike previously published FTIR reflectance studies (which require a Kramers-Kronig analysis to determine the TO/LO phonon peaks), our FTIR ellipsometry measurements allow the direct determination of TO and LO phonon energies as peaks in the dielectric function ϵ and the loss function $1/\epsilon$, respectively.

Magnesium aluminate spinel (MgAl_2O_4) belongs to the cubic O_h^7 space group and has two formula units per primitive cell. Of its 39 optic modes, factor group analysis [2] shows that there are only four IR-active modes with T_{1u} symmetry. The lattice dynamics of spinel has long been controversial and differences have been found between natural crystals (which are believed to be fully ordered) and synthetic crystals (which often contain a small amount of Mg/Al disorder).

A good description of the dielectric functions of these materials can be found using a sum of Lorentz oscillators (for the TO phonons in our spectral range) and two poles for electronic and low-energy phonon absorption outside of our spectral range. A factorized model [3] with LO/TO phonon pairs and a UV pole yields even better agreement with the data. The classical Lorentz model assumes a frictional force proportional to the velocity of the atoms resulting in a single broadening parameter, while the Lowndes model [3] takes into account the anharmonic phonon decay and assigns independent broadening parameters to the LO and TO phonons. Our FTIR ellipsometry measurements yield LO and TO parameters (energies, broadenings, and oscillator strengths) with unprecedented accuracy, far exceeding those from previous FTIR reflectance results. We will compare our experimental phonon energies with those obtained from *ab initio* density-functional theory for both LaAlO_3 and MgAl_2O_4 .

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Electronic Materials and Processing

Room: 102 A - Session EM+AS+PS+TF-ThM

Materials and Process for Advanced Interconnects I

Moderator: S.W. King, Intel Corporation, E. Mays, Intel Corporation

8:00am **EM+AS+PS+TF-ThM1 Measurement of the Bandgap Energies in Low-k Organosilicates, M. Nichols, University of Wisconsin-Madison, Q. Lin, IBM T.J. Watson Research Center, S. Banna, Applied Materials Inc., Y. Nishi, Stanford University, J.L. Shohet, University of Wisconsin-Madison**

The experimental measurements of the electronic band gap of low-k organosilicate dielectrics are presented and discussed. The measurement of bandgap energies of organosilicates was made by examining the onset of inelastic energy loss in core-level atomic spectra using x-ray photoelectron spectroscopy (XPS). This energy serves as a reference point from which many other facets of the material can be understood, such as the location and presence of defect states in the bulk or at the interface. In order to measure the spectra due to inelastic energy loss, a suitable primary photoelectron peak must be chosen. Although in principle any core-level spectra will exhibit the same inelastic losses, the measured photoelectron intensity must be large enough so that a sufficient signal to noise ratio can be achieved with suitably high resolution. It was determined that the O 1s peak is dominant for both SiO_2 and for the organosilicate films used in this work.

To find the bandgap energy, a linear fit is made to the measured loss spectra curve near the approximate location of onset of inelastic losses. The energy corresponding to the onset of inelastic losses, is found by extrapolating the linear fit line and calculating its intersection with the "zero" level. The bandgap energy is equal to the difference between the core level peak energy and the onset of inelastic losses. For SiO_2 this method yields a bandgap energy of 8.8 eV which is in excellent agreement with the established value of 8.9 eV. Bandgap energies were measured for 644 nm $k=2.75$ as-deposited SiCOH films using the linear extrapolation method, yielding a bandgap energy of $E_g = 7.0$ eV. For 500 nm thick $k=2.65$ SiCOH the bandgap energy was found to be 7.7 eV while for a 325 nm thick, $k = 2.75$ photopatternable low-k (PPLK) dielectric, the bandgap was found to be 8.25 eV.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant CBET-1066231.

8:20am **EM+AS+PS+TF-ThM2 Complementary Porosity Metrologies for Porous Ultra Low-k Material, D. Yang, R. Opila, University of Delaware, V. Pallem, Air Liquide, D. Dutta, D. Gidley, University of Michigan, N. Bhargava, University of Delaware**

As transistor density on integrated circuits doubles as driven by Moore's Law, propagation delays from interconnections at the back-end-of-line (BEOL) have begun to contribute significantly. Low dielectric constant (k) materials, e.g. organosilicate glasses (SiCOH), have been introduced to replace silicon oxide to reduce power consumption and capacitive signal delay. It has been generally agreed that decreasing material density by incorporating porosity is the most feasible means to achieve ultra low k. However, when a higher portion of porogen is introduced, pores tend to aggregate and interconnect, especially when porosity is above percolation threshold. The pore interconnectivity may lead to degradation of mechanical and thermal properties and permit intrusion of moisture, chemical species and sequestering of cleans byproducts. Therefore, characterization and understanding of porosity and pore interconnectivity are important to optimize porous low-k materials. In this work, three non-destructive porosimetry techniques, *Positron Annihilation Lifetime Spectroscopy (PALS)*, *Ellipsometric Porosimetry (EP)* and *X-ray Reflectivity (XRR)*, are applied to characterize porous SiCOH low-k dielectric thin films of different porosity and pore interconnection, results will be analyzed and compared to highlight each technique's advantage and limitation for characterizing porous low-k materials. This study will provide valuable guidance for future porosity characterization, data comprehension, porosity understanding and further structural optimization of porous low-k materials.

The results showed that ellipsometric porosimetry (EP) provides information on open meso-pores accessible to organic solvents but may underestimate porosity without probing pores smaller than the probing organic molecule²; Positron Annihilation Lifetime Spectroscopy (PALS), which probes the amount of free surface and is able to detect micropores but with limitations on analyzing multiple pore size distribution within pore interconnection length; PALS also has unique feature to quantify pore interconnection length by depth-profiling; X-ray Reflectivity (XRR) gives

absolute overall porosity in terms of film density but tends to overestimate porosity and provides few details on pore size distribution.

After comparison, we conclude that each porosimetry technique shows their strengths and limitations due to different physical principles. Information derived from any single porosimetry technique is not sufficient to reveal comprehensive pore information without bias. Therefore, metrology must be carefully selected and complementary techniques are required in order to acquire a full picture of pores.

8:40am **EM+AS+PS+TF-ThM3 Future of Ultra Low-k Materials**, *W. Volksen, T. Magbitang, K. Lioni, G. Dubois*, IBM Almaden Research Center **INVITED**

Integration of porous low dielectric constant materials constitutes a major roadblock in the reliable manufacturing of back end of the line (BEOL) wiring for advanced technology nodes [1]. The two main issues for Ultra low-k (ULK) materials are their low mechanical properties and high sensitivity to plasma induced damage (PID). We have developed a new class of bridged oxycarbosilane (OCS) type materials with unique stiffness [2-4], and a novel process to enable their integration [5,6]. The Post Porosity Plasma Protection (P4) consists of refilling the pores of the fully cured porous ULK with an organic material prior to patterning, integrating the protected ULK and thermally removing the filler at the end of the process. We demonstrate the enormous potential of our integrated solution (materials at $k < 2.4$ and P4 process) on blanket films and its compatibility with integration.

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9:20am **EM+AS+PS+TF-ThM5 Porosity Scaling Strategies for Low-k Films**, *D.J. Michalak, J.M. Blackwell, A. Sengupta, J.S. Clarke, D. Pantuso*, Intel Corporation

Mechanical properties of highly porous low-k films are a key manufacturing concern area. Next generation ILD materials will need to be carefully crafted in order to deliver a needed reduction in dielectric constant while also delivering needed mechanical and chemical stability concerns. We have generated a backbone and porogen system with high chemical stability that allows us to control porosity from 0% to 60% volume and achieve dielectric constant values ranging from 3.4 to 1.6. At a given porosity, Young's modulus values are higher than typical PECVD films, but the amount of improvement decreases as porosity increases. The high porosity and mechanical strength were achieved by tuning the number of reactive crosslinking sites on our oligomeric backbone precursor. Our data are evaluated in light of percolation theory, which sets a theoretical maximum porosity limit for materials made from random mixes of backbone and porogen. Ways around this maximum limit are proposed. Finite Element Modeling of the 0-60% porosity films yielded calculated Young's modulus values very close to observed values when experimental inputs of porosity, pore size, and pore shape were used. Up to 4x improvement in Young's modulus is observed for hypothetical structures containing controlled pore size, shape, and order. Stress contour mapping allows a rapid visualization of the mechanisms at play. Material needs for the next generation ILDs will be discussed in light of these data.

9:40am **EM+AS+PS+TF-ThM6 Ellipsometric Porosimetry Surface Characterization of Oxygen Plasma Damage and κ Repair on Ultra Low κ Dielectrics**, *Z. Sun*, GLOBALFOUNDRIES U.S. Inc., *A. Bondaz, T. Karpowicz, Semilab, V. Seshachalam, S. Srivathanakul, H. Liu*, GLOBALFOUNDRIES U.S. Inc.

Due to its intrinsic weakness of high levels of carbon-containing compounds and open pores, an ultra low- κ film is prone to Back End of Line (BEOL) downstream damage from processes such as ashing, reactive ion etching, wet processing and CMP. With continued scaling beyond the 14nm technology node, κ repair processes become required as an ultimate solution in restoring the dielectric properties and keeping the low κ benefit of low capacitance and power consumption.

Oxygen plasma is widely used in the ashing process of photo resist stripping, which degrades low- κ material and cause dielectric loss. In this study, Ellipsometric Porosimetry (EP) has been applied to characterize the ultra

low- κ surfaces, which are damaged by oxygen plasma and repaired by subsequent hydrocarbon-sourced plasma. The results of the pore size measured by EP shows 1.1nm pore size for a pristine film, 0.4nm for a repaired film and no pores for a damaged film. The conclusion from these readings indicate that the damaged film has a dense crust on the top of the film which prevents adsorption of the solvent used in EP. The repair process reopens the pore but not completely since it shows a significantly smaller pore size than the pristine film. When low- κ films undergo a heating process, the pristine film shows an approximate linear behavior of thermal expansion, while the damaged film shows thickness shrinkage, which could be explained by the desorption of the -OH containing species formed due to oxygen plasma exposure. The repaired film shows the same trend as the pristine film, with the same extracted Coefficients of Thermal Expansion (CTE) as the pristine film. The penetration of plasma repair has been identified as deep as 30nm through film stack model fitting.

This extensive study proves the κ repair process is taking effect as well as proving Ellipsometric Porosimetry is capable and sensitive enough to measure the film property changes statically and dynamically.

10:40am **EM+AS+PS+TF-ThM9 Pore Stuffing to Enable Interconnect Scaling**, *J.D. Bielefeld, M. Chandhok, J.S. Clarke, C.J. Jzewski, K. Singh, A.M. Myers, J.M. Torres, R. Turkot*, Intel Corporation

To lower interconnect signal delay, the industry continues to work on the integration of low-k interlayer dielectrics (ILD). Momentum has slowed in recent years due to the challenges of working with porous thin films. The pores in the ILD can lead to damage and increased roughness during patterning, and can allow precursor penetration during the metal barrier deposition. Low-k ILDs ($k \sim 2.0$) exhibit 40-50% porosity with interconnected pores with pore size at approximately 2nm+. These challenges are currently reducing interconnect reliability and inhibiting combined capacitance and resistance scaling.

Two approaches have been investigated to mitigate the integration issues with porous dielectrics. The first is pore sealing, in which a non-porous layer is added to the porous ILD's surface to enhance adhesion and to prevent metal penetration during barrier deposition. The down-side of pore sealing is that it does not address the issue of damage and profile roughness during the patterning process.

The second approach is pore stuffing, in which a sacrificial material is infiltrated into the pores of a fully cured ILD. This process generates a non-porous material with increased mechanical properties. The benefits of a non-porous material are utilized during both patterning and metallization. Once the metallization process is complete the sacrificial material is removed to restore the properties of the low-k ILD.

In this paper, we will discuss the challenges of finding a pore stuffing material that can fill the pores of the ILD, that can remain in place during dual damascene processing and that can be removed low-k ILD post metal deposition. Next we will show step by step how pore stuffing improves trench profiles, enhances resistance to wet cleans damage, and eliminates metal precursor penetration. Finally the successful implementation of this process into a dual damascene process flow will be shown.

11:00am **EM+AS+PS+TF-ThM10 Molecular Layer Deposition of Organic Films for Nanoelectronics Applications**, *S.F. Bent*, Stanford University **INVITED**

Many challenges exist in forming the nanostructured materials that will be needed for future electronics technologies. New approaches are required in both the materials and the processing methods to achieve the required atomic-scale level of control. This presentation will focus on the potential for molecular layer deposition (MLD) to solve some of the technological challenges in nanoelectronics applications. MLD, like the analogous process of atomic layer deposition, utilizes an alternating sequence of self-limiting reactions, and it can be used to deposit conformal, tunable organic films with controllable thicknesses down to the sub-nanometer scale. In our studies, a variety of nanoscale organic films have been deposited by MLD via urea coupling chemistry and other related coupling chemistries. Different backbones have been used to tune the properties of the organic films, which are attached covalently to the underlying substrate. Incorporation of blended and nanolaminated films, which can allow for the films properties to be optimized at a molecular level, has also been explored, and the films have been characterized by a variety of experimental techniques.

A potential application for MLD films is for advanced interconnects. To meet the aggressive demands of interconnect scaling, future devices will require ultrathin, smooth, conformal copper diffusion barriers and seed layers, motivating the development of new barrier layer materials. Organic films are one promising class of materials that have received interest as a possible solution. We have explored the use of MLD to form nanoscale organic thin films for barrier layer applications. The technique allows tailoring of the film properties to optimize desirable barrier properties, such

as density, copper surface adhesion, thermal stability, and low copper diffusion. We will describe the copper diffusion barrier properties of the nanoscale organic films as tested by adhesion, annealing, and microscopy studies. Other applications of the MLD films for nanoelectronics, including use as resist materials for extreme ultraviolet (EUV) lithography and as surface modification layers for subsequent materials deposition, will also be presented.

11:40am **EM+AS+PS+TF-ThM12 Surface Photoconductivity of Low-k Organosilicates Induced by Plasma Vacuum Ultraviolet Radiation, H. Zheng, D. Pei, M. Nichols**, University of Wisconsin-Madison, **S. Banna**, Applied Materials Inc., **Y. Nishi**, Stanford University, **J.L. Shohet**, University of Wisconsin-Madison

Charging during plasma processing of VLSI/ULSI devices can cause degradation of dielectrics and is a leading cause of damage in semiconductor devices. Thus, a search for a proper method to limit and deplete charge in dielectric materials, especially low-k dielectric materials, (SiCOH) has received great interest. In this work, the temporary increase in the surface conductivity of SiCOH during exposure to vacuum-ultraviolet radiation is investigated and compared with similar measurements for SiO₂¹. To measure this, patterned titanium "comb structures" were deposited on thin SiCOH films and exposed to synchrotron radiation. VUV-induced currents along the surface of the layer between the titanium fingers of the comb structure were measured by biasing the comb structure through electrical connections from the test structure to outside circuitry. By measuring the I-V characteristics of the comb test structure under a constant flux of VUV light, we determined that, for low electric fields, the measured current density and applied electric field are linearly proportional. However, because the SiCOH samples used here are relatively thin, as the electric field increases, the photoinjection current from the substrate becomes large and then dominates the measured VUV-induced current. Hence, it is possible to generate a self-consistent VUV-induced IV characteristic only by using low applied electric fields. Based on these measurements, the surface conductivity can be found. Specifically, under VUV radiation with photon energies between , the surface conductivity of the SiCOH films materials increases by at least one order of magnitude compared with the surface conductivity in the absence of radiation. This increase can be beneficial in limiting charging damage of dielectrics by depleting the plasma-deposited charge, which holds the potential to decrease processing-induced plasma damage to semiconductor devices significantly.

¹ C.Cismaru, J.L. Shohet and J.P. McVittie, *Applied Physics Letters*, **71** 2191 (2000).

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Plasma Science and Technology

Room: 102 B - Session PS+AS+NS+SS-ThM

Plasma Synthesis of Nanostructures

Moderator: R.M. Sankaran, Case Western Reserve University

8:00am **PS+AS+NS+SS-ThM1 Nanoscale Interface Engineering of Silicon Nanocrystals by Non-equilibrium Microplasma, V. Svrcek**, Advanced Industrial Science and Technology (AIST), Japan **INVITED**

Silicon nanocrystals (Si-ncs) created vast interests and Si-ncs interfaces are at the basis of application in water splitting, for bio-imaging and may open up great opportunities for the development of most advanced technologies. For instance, in photovoltaic community enormous interests is mainly due to their enhanced multiple exciton characteristics. The fundamental aspects of exciton dissociation are highly important to improve the efficiency of solar cells and therefore the employment of Si-ncs in a range of applications requires careful investigation on the surface conditions. Indeed, the interplay of quantum confinement with surface effects reveals a complex scenario, which can strongly affect of Si-ncs properties and prediction of their corresponding behaviour. In this context, a variety of carefully surface-engineered Si-ncs are highly desirable both for understanding of Si-ncs photo-physics and for their successful integration in application devices. Surface surfactant free functionalization techniques that can assess the functionalities of the Si-ncs interface need to be developed so that efficient charge transport and excitons dissociation could be achieved. In this talk we firstly highlight a selection of theoretical efforts and experimental surface engineering approaches. Secondly we present our results on surfactant free surface engineering of Si-ncs, which have utilized novel microplasma-liquid interactions. The possibilities of surface engineering and tuning

overall Si-ncs properties by two independent techniques will be pointed out. Particularly, we will show that the atmospheric pressure RF and DC microplasmas in liquid media offer a wide range of opportunities for Si-ncs surface engineering due to multiple mechanisms induced by the microplasma process and more efficient electron driven non-equilibrium liquid chemistry. The flexibility and results on superior capabilities of the microplasma-based surface engineering approach will be presented. Then, an influence of Si-ncs surface engineering on photovoltaic based devices and the possibilities of enhancement optical density and role of Si-ncs surface engineering on integration within nanotubes will be shown. Finally the potential for scaled-up to achieve large scale surface engineering as would be required for industrial applications will be discussed as well.

8:40am **PS+AS+NS+SS-ThM3 Single Step Plasma Synthesis of Core-shell Group IV Nanoparticles, R.P. Chaukulkar***, Colorado School of Mines, **K. de Peuter**, Eindhoven University of Technology, Netherlands, **P. Stradins**, National Renewable Energy Laboratory, **S. Agarwal**, Colorado School of Mines

There has been an increased interest in group IV nanoparticles (NPs) for a variety of applications including photovoltaics, lithium ion batteries, and bio-imaging. The properties of these quantum-confined NPs are governed by their size as well as the surface passivating layer. Si NPs, 3-7 nm in size, were synthesized in a tubular, capacitively-coupled, radio-frequency SiH₄/Ar plasma at pressures ranging from 5-8 Torr. The H-terminated surface of the as-synthesized Si NPs is highly reactive, and requires surface passivation to prevent oxidation. We have developed a single-step synthesis and in-flight surface passivation technique wherein we use a dual-plasma setup, which consists of a second capacitively-coupled C₂H₂ plasma, downstream from the SiH₄/Ar synthesis plasma. The Si NPs can be coated with amorphous carbon (a-C) to obtain core-shell nanostructures, with a thin SiC interface between Si and a-C. These core-shell NPs are transported by flow into a surface analysis chamber, which is equipped with *in situ* attenuated total reflection Fourier transform infrared and photoluminescence spectroscopy setups to determine the surface composition and the optical band gap of the NPs, respectively. The NPs are also extensively characterized using *ex situ* x-ray diffraction, Raman spectroscopy, and transmission electron microscopy (TEM). The thickness of the coating, determined from TEM, is ~2-4 nm. We have also studied the effect of varying the C₂H₂ plasma parameters on the structure and composition of the a-C coating and the SiC interface. This plasma synthesis and passivation technique has been extended to other group IV NPs such as Ge and Sn, which are less likely to have a carbide interface.

9:00am **PS+AS+NS+SS-ThM4 On the Structure of Non-Thermal-Plasma Produced Nanocrystals, T. Lopez, L. Mangolini**, University of California, Riverside

The use of continuous flow non-thermal plasma reactor for the formation of silicon nanoparticles has attracted great interest because of the advantageous properties of the process [1]. Despite the short residence time in the plasma (around 10 milliseconds), a significant fraction of precursor, silane, is converted and collected in the form of nanopowder. The structure of the produced powder can be tuned between amorphous and crystalline by adjusting the power of the radio-frequency power excitation source, with high power leading to the formation of crystalline particles [2]. Numerical modelling suggests that higher excitation power results in a higher plasma density, which in turn increases the nanoparticle heating rate due to interaction between ions, free radicals, and the nanopowder suspended in the plasma [3]. An understanding of the mechanism that leads to the crystallization of the powder while in the plasma is lacking. In this work, we present an experimental investigation on the crystallization kinetic of plasma-produced amorphous powder. Silicon nanoparticles are nucleated and grown using a non-thermal plasma reactor similar to the one described in [1], but operated at low power to give amorphous nanoparticles. The particles are then extracted from the reactor and flown through a tube furnace capable of reaching temperatures up to 1000°C. Raman and TEM have been used to monitor the crystalline fraction of the material as a function of the residence time and temperature. A range of crystalline percentages can be observed from 750 °C to 830 °C. We have also used *in-situ* FTIR to monitor the role of hydrogen on the crystallization kinetic. It has been proposed that that hydrogen induced crystallization is the mechanism for deposition of microcrystalline silicon thin films in PECVD systems. We find that the plasma-produced amorphous silicon powder is rich with surface SiH_x species, but no detectable signature from bulk Si-H bonds has been observed. A discussion of particle growth and plasma-particle interaction will be presented with its relation to the overall effect on crystallization mechanisms.

*** Coburn & Winters Student Award Finalist**

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2. O. Yasar-Inceoglu, T. Lopez, E. Farshihagro, and L. Mangolini, *Silicon nanocrystal*

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nonequilibrium in dusty plasmas. Physical review E **2009**, 79, 026405 1-8.

9:20am **PS+AS+NS+SS-ThM5 Detection of Nanometer Scale Ni Clusters Formed in an Atmospheric Pressure DC Microplasma by Ion Mobility Spectrometry**, *C.J. Hogan*, University of Minnesota, *A. Kumar*, Case Western Reserve University, *S. Kang*, *C. Larriba-Andaluz*, *H. Ouyang*, University of Minnesota, *R.M. Sankaran*, Case Western Reserve University

Using a high resolution differential mobility analyzer (1/2-mini DMA, Nanoengineering) coupled to a Faraday cage electrometer for ion mobility spectrometry, we have investigated the formation of Ni clusters in a DC atmospheric pressure Ar microplasma. To produce Ni clusters, nickelocene (bis(cyclopentadienyl)nickel) vapor was continuously introduced into the microplasma by sublimation of a heated solid powder into an Ar gas flow. Particles were nucleated, grown, and rapidly quenched to limit their diameter to less than ~10 nm. Prior to mobility measurement, a steady-state charge distribution of the aerosol particles was achieved via diffusion charging with background gas ions produced in a Kr-85 source (TSI, Inc.). Both positive and negative mobility distributions were measured. A background high intensity peak around ~0.75 nm equivalent "mobility diameter", corresponding to the ions produced by the Kr-85 source, was always observed. The introduction of nickelocene vapor in the microplasma resulted in a lower intensity distribution of particles, spanning from the peak corresponding to Kr-85 generated ions to 10 nm in mobility size. Under all circumstances, the mobility distribution from the ion peak to the largest produced particles was continuous, indicating the microplasma reactor can form stable Ni clusters below 2.0 nm in size. To obtain structure-mobility relationships, density functional theory and gas molecule scattering calculations were carried out. The nanoparticles were also collected by electrostatic precipitation and further characterized by atomic force microscopy to confirm their size and distribution. These results confirm a that a continuous distribution of particles is formed in microplasma processes down to less than 1.0 nm which could have both fundamental and technological implications ranging from the study of particle formation in the vapor phase to novel applications of quantum confined materials.

9:40am **PS+AS+NS+SS-ThM6 One-step Synthesis of Gold Bimetallic Nanoparticles with Various Metal Compositions**, *M.A. Bratescu*, *N. Saito*, Nagoya University, Japan

In our group, Solution Plasma Processing (SPP) is a useful and simple method for metal NPs (nanoparticles) synthesis [1, 2]. In the present work, we demonstrate a special merit of the SPP method for the fabrication of bimetallic NPs using a combination of the reduction reaction of the metal (M) ion to the neutral state, while simultaneously eroding the electrodes during the discharge, which generates the second metal in the structure of the bimetallic NPs [3].

The gold bimetallic NPs were synthesized by alloying gold with various types of metals, which are divided in four categories: (i) divalent *sp* metals, Zn and Cd, (ii) trivalent *sp* metals, Ga and In, (iii) 3*d* metals Fe, Co, Ni, and Cu, and (iv) 4*d* metals Pd and Ag. We used SPP between two gold electrodes immersed in a nitrate solution of the corresponding metal M. We studied the optical properties of the gold nanoalloys, as well as their crystallinity, composition, size and morphology, and we have evaluated the interaction of various gold bimetallic NPs with free radicals for possible consideration as catalysts. SPP characterization has been done using electrical and optical probes. We found that the properties of the gold bimetallic NPs are connected with the category to which the metal belongs. We analyzed that the amount of the intermetallic compound in the composition of the gold bimetallic NPs depends on the electrochemical potential and the electron density of the Wigner-Seitz cell. The obtained gold bimetallic NPs using one step in Solution Plasma have sizes in the range from 5 to 20 nm. The difference in electronegativity between gold and the other metal was the main reason for the formation of the intermetallic compounds found in the composition of the gold bimetallic NPs. This work was supported in part by Kakenhi, Challenging Exploratory Research, JSPS, Japan.

[1] M.A. Bratescu, et al., J. Phys. Chem. C **115** (2011) 24569.

[2] S.P. Cho, et al., Nanotechnology **22** (2011) 455701.

[3] M.A. Bratescu, et al., J. Alloys and Compounds **562** (2013) 74.

10:40am **PS+AS+NS+SS-ThM9 Synthesis of Platinum Nanoparticles on Carbon Powder by the Means of an RF Plasma Torch for Fuel Cells Applications**, *D. Merche*, *T. Dufour*, Univ. Libre de Bruxelles, Belgium, *L. Devant*, Facultés Univ. Notre Dame de la Paix, Belgium, *F. Deschamps*, Univ. de Liège, Belgium, *J.-J. Pireaux*, *L. Houssiau*, Facultés Univ. Notre Dame de la Paix, Belgium, *N. Job*, Univ. de Liège, Belgium, *F.A.B. Reniers*, Univ. Libre de Bruxelles, Belgium

The grafting of noble metal nanoparticles on porous carbon supports has attracted a great interest over the last few years, due to potential applications in Proton Exchange Membrane Fuel Cells (PEMFC). Plasma processes for the synthesis of such electrodes could be a major asset for the production of the fuel cell elements at lower cost.

In this study, Pt nanoparticles are synthesized from the decomposition of Platinum (II) acetylacetonate [Pt(acac)₂] and deposited on porous carbon by the means of an RF atmospheric plasma torch running with argon in an open air environment. This one single step technique is very simple, fast and robust. It also presents substantial economic advantages, such as the non requirement of a high-vacuum and the possibility to easily implement this process in a continuous production line. The Pt nanoparticles were principally grafted on carbon-black powder. Some tests were also conducted on Carbon Xerogel matrices presenting well-controlled porosity.

The organometallic-carbon powder mixture pressed on a copper tape was treated in the post-discharge of the Ar plasma torch. A kinetic study has been carried out by XPS to evaluate the optimal exposure time to the post-discharge required for synthesizing a significant amount of Pt nanoparticles. 6% of Pt was detected after only 30 seconds of plasma treatment, and 14% after 600 seconds. According to the fitting of the Pt XPS peaks, the most intense component of the Pt for the sample treated by plasma was the Pt(0). 68% of the platinum was under metallic form after 30 seconds of plasma treatment, and 78 % after 600 seconds.

The effect of the distance between the powder and the torch, and the addition of a small quantity of hydrogen to the vector gas was studied by XPS regarding the elemental composition and the oxidation state of the platinum nanoparticles. A comparison with Pt synthesized in a controlled atmosphere was also realized. For a study more focused on the PEMFC applications, the powder mixture was overlaid on a Gas Diffusion Layer (GDL), namely Carbon Toray Paper (CTP), before being exposed to the Ar post-discharge.

The size and the dispersion of the nanoparticles grafted on carbon black powder or on carbon Xerogel were observed by a FEG-SEM and by TEM.

11:00am **PS+AS+NS+SS-ThM10 Growth of Nanocomposites on Heat-Sensitive Polymers using Cold, Dielectric Barrier Discharges at Atmospheric Pressure**, *J. Profili*, Université Paul-Sabatier, France and Université de Montreal, Canada, *N. Gherardi*, CNRS-LAPLACE, France, *L. Stafford*, Université de Montreal, Canada

Cold, atmospheric-pressure plasmas have already demonstrated their potential for homogeneous thin film deposition in polymers functionalization. In order to achieve multifunctional properties, a new challenge is the plasma-assisted deposition of nanocomposite coatings. This contribution is focused on the growth of nanocomposites based on TiO₂ nanoparticles embedded in a silica-like matrix with the objective of synthesizing barrier layers with improved resistance to UV irradiation. Experiments were carried out in a parallel plate dielectric barrier discharge with the substrate placed on the bottom electrode. The gas mixture is composed of either N₂ or He as the carrier gas, a mixture of hexamethyldisiloxane, and either nitrous oxide (for experiments in N₂) or O₂ (for experiments in He) for the growth of the SiO₂ matrix, and TiO₂ nanoparticles which are introduced by nebulizing stable colloidal solutions. Preliminary results show that TiO₂ nanoparticles can successfully be incorporated in the film. In addition, as in low-pressure plasma conditions, electrostatic forces were found to play a very important role on the transport of nanoparticles in the discharge. As a result, an appropriate tuning of the applied voltage waveform (shape, amplitude and frequency) was found to directly impact the spatial distribution of nanoparticles in the film.

11:20am **PS+AS+NS+SS-ThM11 Fabrication of Asymmetric Nanopores by Pulsed PECVD**, *S.S. Kelkar*, *C.A. Wolden*, Colorado School of Mines

The field of nanopore fabrication has attracted a lot of attention recently due to their potential application in DNA sequencing, ionic field effect transistors, and detection and separation of biomolecules and nanoparticles. The objective of our research is to develop a simple approach for large area fabrication of nanopores (pore size ~ 1–10 nm) with atomic level precision.

In this work, we first employ relatively large template structures (~ 100–250 nm) produced by track-etching or e-beam lithography. The pore size is then refined to the desired level by deposition of material using pulsed plasma enhanced chemical vapor deposition (PECVD). Pulsed PECVD has been developed as an alternative to atomic layer deposition (ALD) to deliver self-limiting growth of oxides like alumina and silica. Pulsed PECVD has two growth components that act sequentially: ALD-like growth during the plasma off step ($\gamma \sim 0$); and PVD-like growth during the plasma on step ($\gamma \sim 1$), where γ is the reactive sticking probability. The ALD contribution is constant at $\sim 1 \text{ \AA/pulse}$ whereas the PECVD contribution can be typically varied from 0.5 - 5 \AA/pulse by appropriate control of operating conditions. The degree of conformality in pulsed PECVD can be engineered by controlling the relative contribution of these 2 growth components. As such this technique can produce novel morphologies that are distinct from those produced by conventional deposition processes. We have developed feature scale models to predict the pore closure phenomenon in pulsed PECVD. This model successfully predicts experimentally observed profiles in features such as trenches and cylinders. The model findings will enable us to determine optimal operation conditions for obtaining the desired nanopore opening and geometry. Flux experiments on nanopore-based membranes are further employed to validate the feature scale models. Such well-defined nanopores can serve as an ideal platform for rigorous evaluation of hindered transport at the nanoscale.

11:40am **PS+AS+NS+SS-ThM12 Microplasma Reduction of Metal-Organic and Metal-Polymer Films for Single-Step Fabrication of Flexible, Conductive Patterns**, S. Ghosh, R. Yang, C.A. Zorman, P. X.-L. Feng, R.M. Sankaran, Case Western Reserve University

In situ approaches to synthesizing metal nanoparticles from metal-organic or metal-polymer films have recently emerged as a simple and viable method to fabricating flexible, conductive patterns.^{1,2} In general, a metal precursor is mixed or reacted with an organic or monomer, cast as a film, and exposed to ultraviolet, laser, heat, or electron beam (e-beam). Recently, we have demonstrated that an atmospheric-pressure microplasma can be similarly used to initiate reduction of metal ions and formation of metal nanoparticles in polymer films.³ In this study, we present electrical characterization of the reduced lines and show that conductive patterns are achieved similar to other methods including e-beam irradiation.

Polymer films containing ionic metal precursors were prepared by first dissolving metal salts [e.g., silver nitrate (AgNO_3), palladium acetate ($\text{Pd}(\text{OAc})_2$] with polymers [e.g., polyvinyl alcohol (PVA), polymethylmethacrylate (PMMA)] in solution. The solvent was chosen according to the metal salt-polymer system. For AgNO_3 and PVA, we used a 1:1 ratio of water:ethanol, and for $\text{Pd}(\text{OAc})_2$ and PMMA, acetonitrile was used. The mixed metal-organic solutions were drop cast or spin coated onto Si substrates to form thin films (100nm~1 μm thick). The films were dried in vacuum and then exposed to the microplasma process. An Ar microplasma was formed by applying DC power to a stainless steel capillary tube and the substrate holder. Patterns were generated by scanning the microplasma at constant discharge current. After exposure, the films were peeled off from the substrate and transferred to a glass substrate. The conductivity was measured using a two point probe method. The as-prepared films were also characterized by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDX) to confirm metallization (*i.e.*, reduction) over the exposed areas.

Our results show that plasma exposure leads to conductive patterns on a free-standing flexible substrate. SEM and EDX confirm the reduction of metal ions to metal nanoparticles. We have also compared these results with exposure to an e-beam. In the case of the plasma, the polymer is removed, probably due to oxidation, whereas the e-beam causes conformational changes to the polymer. The effects of annealing following exposure to increase the conductivity of the films will also be discussed.

References:

1. B. Radha et al., J. Am. Chem. Soc. 133, 12706–12713 (2011).
2. S. W. Lee et al., Adv. Funct. Mater. 21, 2155-2161 (2011).
3. S. W. Lee et al., Macromolecules 45, 8201–8210 (2012).

Plasma Science and Technology Room: 104 C - Session PS-ThM

Plasma Modeling

Moderator: D.J. Economou, University of Houston

8:00am **PS-ThM1 Molecular Dynamics Analysis of Si Etching in HBr-based Plasmas: Ion Incident Energy and Angle Dependence**, N. Nakazaki, Y. Takao, K. Eriguchi, K. Ono, Kyoto University, Japan

Profile anomalies and surface roughness are now critical issues to be resolved in the plasma etching of nanometer-scale microelectronics devices, which in turn requires a better understanding of the effects of the ion incident energy and angle on surface reaction kinetics. For example, the line edge and line width roughness on feature sidewalls and the roughness on bottom surfaces of the feature are assumed to be caused by the angular distribution of incident ions onto feature surfaces. In addition, incident neutral radicals also affect the surface reaction kinetics and thus etching characteristics achieved. This paper presents a classical molecular dynamics (MD) simulation of Si etching in HBr-based plasmas with different ion incident energies and angles, by using an improved Stillinger-Weber interatomic potential model for Si/H/Br system interactions. Emphasis is placed on the surface structure and the yield and stoichiometry of products depending on the ion incident energy, angle, and neutral radical-to-ion flux ratio.

In the MD simulation, a target substrate Si(100) was placed in the simulation cell, which was a square 32.58 \AA on a side and initially contained 1440 Si atoms ($6.78 \times 10^{14} \text{ atom/cm}^2$) in a depth of 26 \AA . Energetic ions and low-energy neutral radicals were injected toward the surface from randomly selected horizontal locations above the target. We assumed that the plasma of interest consisted of HBr^+ ions and H and Br neutrals. The ion incident energy was in the range $E_i = 20\text{--}300 \text{ eV}$ and the incident angle was in the range $\theta_i = 0\text{--}90^\circ$. The neutral radical-to-ion flux ratio was $\Gamma_n/\Gamma_i = 0$ and 100. In addition, we sometimes added a layer of Si atoms at the bottom of the simulation cell, to maintain the number of target atoms during etching. The yield and stoichiometry of products, and the surface structures were analyzed by averaging more than 1000 impacts after the surface and etching characteristics had become statistically stable.

Numerical results indicated that the thickness of the surface reaction layer (SiH_xBr_y layer) decreases with increasing θ_i , because of decreased penetration depth of incident ions at large θ_i , which is less significant for $\Gamma_n/\Gamma_i = 100$ than for $\Gamma_n/\Gamma_i = 0$ at each E_i incidence, owing to increased desorption of reaction products therefrom at increased Γ_n/Γ_i as a result of enhanced etching reactions. Moreover, the Si yield is larger for $\Gamma_n/\Gamma_i = 100$ than for $\Gamma_n/\Gamma_i = 0$, and correspondingly, the amount of volatile etch products containing H atoms is larger for $\Gamma_n/\Gamma_i = 100$ than for $\Gamma_n/\Gamma_i = 0$.

8:20am **PS-ThM2 MD Simulations of Pulsed Chlorine Plasmas Interaction with Ultrathin Silicon Films for Advanced Etch Processes**, P.D. Brichon, E. Despiau-Pujo, G. Cunge, M. Darnon, O. Joubert, Cnrs/ujf/ Cea - Ltm, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous-wave plasma processes are not able to selectively etch ultrathin films without damaging the active layers of advanced nanoelectronic devices (e.g. FDSOs, FinFETs). In order to achieve a uniform/smooth etching of sub-nm thick materials, one possible alternative is to use pulsed-plasma discharges which exhibit lower average ion energies, thus minimizing surface damage when necessary. Pulsing the plasma consists in switching on and off the RF power, which introduces two additional parameters, the pulsation frequency and the duty cycle, i.e. the ratio between the pulse on-time and the total pulse duration. This latter has been shown to control the dissociation rate of the plasma i.e. the proportion of atomic species (Cl , Cl^+) relative to that of molecular species (Cl_2 , Cl_2^+). However, the interactions between reactive pulsed plasmas and surfaces are so complex that the efficient development of new processes requires numerical simulations. Therefore, we propose to develop Molecular Dynamics (MD) simulations to study the silicon-chlorine system under pulsed plasma conditions. These simulations can help to understand the precise role of the ion energy in plasma-surface interactions, as well as the relationship between the flux/energy of reactive species (ions, radicals) bombarding the surface and its structural/chemical modifications. To understand the impact of the dissociation rate in pulsed plasma processes, we first compare the effects of atomic (Cl , Cl^+) versus molecular species (Cl_2 , Cl_2^+) bombardment on the silicon substrate. All simulations show an initial rapid chlorination of the surface followed by the formation of a stable SiCl_x mixed layer and a constant etch yield at steady state. Regarding the role of the ion energy, it appears that for most etch features (chlorine uptake, SiCl_x layer thickness, nature of etch products), bombarding the surface with X eV Cl^+ is equivalent to bombarding it with 2X eV Cl_2^+ . This

mathematical relation does not hold for the etch rate, which is larger for atomic bombardment (Cl^+) at low energy (5-10eV) but more important for molecular bombardment (Cl_2^+) at high energy (50-100eV). Comparisons with experiments and mechanisms responsible for these behaviors will be discussed during the presentation. The influence of both the ion-to-radical flux ratio and the duty cycle on the dynamics/characteristics of the etch (yield, products) and on the surface evolution (structure, chemical composition) will also be presented.

8:40am **PS-ThM3 Control of SiO_2 Etch Properties by Pulsed Capacitively Coupled Plasmas Sustained in $\text{Ar}/\text{CF}_4/\text{O}_2$.** *S.-H. Song, M.J. Kushner*, University of Michigan

In the fabrication of microelectronics devices, the performance and quality of the devices are ultimately determined by the energy distribution of charged particles and radicals in the plasma. High aspect ratio dielectric etching in microelectronics fabrication using dual frequency capacitively coupled plasmas (DF-CCPs) continues to be challenged to optimize the fluxes and energy distributions of radicals and ions to the wafer. Pulsed power is one technique being investigated to achieve these goals. In one configuration of DF-CCP, the high frequency (*HF*) power is applied to the upper electrode and low frequency (*LF*) power is applied to the lower electrode serving as the substrate which is serially connected through a blocking capacitor generating self dc bias. In this presentation, ion energy distributions, fluxes to the wafer, and SiO_2 etch properties in a pulsed DF-CCP sustained in $\text{Ar}/\text{CF}_4/\text{O}_2$ are discussed with results from 2-dimensional plasma hydrodynamics and feature profile models. The ion energy distribution (IED) can be uniquely manipulated by either pulsing the *LF* or *HF* power for a given size of the blocking capacitor (BC). During the pulse, the dc-bias can have a time variation – small BC produces more time variation than large BC. This time variation in the dc bias provides an additional control mechanism for the IED. In this paper we report on a computational study of IEDs and SiO_2 etch profiles in DF-CCPs. To investigate this coupling we applied a pulsed format for *HF* and *LF* power with different duty cycles and blocking capacitances. We found that high energy ions are dominant when pulsing *HF* power and low energy ions are dominant when pulsing *LF* power. Smaller BC generally broadens the IED. We also found that the ratio of F/CF_x ($x = 1 - 3$) fluxes increases by pulsing either the *HF* or *LF* however the effect is more sensitive to pulsing *HF* power. Control of etch profiles will be demonstrated by combinations of pulsing *HF* and *LF* power, and BC. For example, bowing and undercut may occur when pulsing *HF* while these effects are suppressed by pulsing *LF*. The propensity for twisting is less when pulsing *LF*.

* Work supported by the Department of Energy Office of Fusion Energy Sciences, the Semiconductor Research Corp. and National Science Foundation.

9:00am **PS-ThM4 Accuracy of the Step Sheath Approximation.** *M.A. Sobolewski*, NIST

In modeling plasma sheaths, it is useful to approximate the electron density profile by a sharp, step-like drop between a neutral (or quasineutral) region and an electron-free region. This approximation allows rapid and efficient numerical calculations of sheath properties, and, when combined with other assumptions, allows predictions for sheath properties to be calculated analytically. Nevertheless, the approximation must result in some loss of accuracy. Here, the accuracy of the step approximation was investigated by comparisons with exact solutions for Poisson's equation in the sheath and with experimental measurements of current and voltage waveforms and ion energy distributions. The measurements were performed in pure argon gas and argon mixtures in a radio-frequency (rf) biased, inductively coupled plasma reactor. Experimental conditions were chosen to cover the intermediate-frequency regime, where the rf period is comparable to ion transit times and the ion current oscillates strongly during the rf cycle. In general, the errors introduced by the step approximation were small but not negligible. The displacement current and time-dependent ion current were both affected by the step approximation, resulting in errors that are more apparent in the phase of the sheath impedance than in its magnitude. The effects on ion energy distributions are most noticeable in the amplitude of the low-energy peak, which is sensitive to the choice of boundary conditions on the plasma side of the step. Using the exact Poisson solution in place of the step approximation results in a modest improvement in the agreement with experiment.

9:20am **PS-ThM5 Multi-dimensional Modeling of Industrial Plasma Processing Systems.** *S. Rauf, J. Kenney, A. Agarwal, A. Balakrishna, M.-F. Wu, K. Collins*, Applied Materials Inc. **INVITED**

Plasma processing is widely used in the semiconductor industry for thin film etching and deposition, modification of near-surface material, and cleaning. Several factors have made plasma modeling critical for plasma processing system design in recent years including the necessity to generate

uniform plasmas over large substrates while fabricating sub-20 nm devices, increased plasma system cost and complexity, and reduced development time-scales. Using examples from recent design and analysis work, this paper describes the current status of multi-dimensional plasma modeling in the semiconductor industry. Areas warranting further research are also discussed. Most industrial design work is done using fluid plasma models due to their maturity, robustness, and computational speed relative to other techniques. Hybrid codes with Monte Carlo simulation of kinetic phenomena (e.g., secondary and beam electrons) are also utilized. Several examples of the use of these fluid plasma models to industrial hardware and process design are discussed, including analysis of the effect of azimuthally asymmetric components on plasma non-uniformity in capacitively coupled plasmas (CCP), the effect of magnetic field on plasma non-uniformity in magnetized CCPs, and the dynamics of synchronously pulsed inductively coupled plasmas. With growing use of very high frequency radio-frequency sources and increasing plasma dimensions, electromagnetic effects have become pronounced in plasmas. A related issue is modeling of the strong influence of the distributed external electromagnetic circuit (e.g., transmission line, antenna feed) on the plasma and its spatial structure. Computational techniques that are used to treat electromagnetic effects in multi-dimensional plasma models along with examples are discussed. Many plasma processes use pressures < 1 Pa. At these low pressures, fluid assumptions break down and kinetic effects become important. An important unsolved problem is how to model these low pressure plasmas accurately in fluid plasma models. Fully kinetic models are more accurate, but their computational cost and lack of robustness remain an issue. Initial efforts at improving fluid plasma models through comparison with particle-in-cell modeling results and experiments are described.

10:40am **PS-ThM9 Self-Consistent Simulations of the Radial Line Slot Antenna Plasma Source.** *P. Ventzek*, Tokyo Electron America, *R. Upadhyay*, Esgee Technologies Inc., *M. Aita, J. Yoshikawa, T. Iwao, K. Ishibashi*, Tokyo Electron Ltd., *L. Raja*, University of Texas at Austin

The radial line slot antenna plasma source couples microwave power through a slot antenna structure and window to a plasma characterized by a generation zone adjacent to the window and a diffusion zone that contacts a substrate. The diffusion zone is characterized by a very low electron temperature. This property renders the source useful for soft etch applications and thin film processing for which low ion energy is desirable. Frequently simulations of the source employ a quasi-neutral plasma model. These are unable to represent the impact of an rf bias applied to a substrate. Furthermore the presence of a time-varying biased potential impacts the transport of charged particles from the zone in which they are created through the diffusion zone to the wafer. At some pressures and powers secondary plasmas may be created. In this presentation we report self-consistent simulations of the source employing a drift-diffusion approximation or variants of this approximation. A test particle Monte Carlo simulation will be used to illustrate the evolution of the electron energy distribution function at different locations in the source. We relate the test particle experiments to electron energy distribution functions derived from solutions of the Boltzmann Equation.

11:20am **PS-ThM11 Feature Profile Simulator with Atomic Mono-Layer Resolution Capability.** *P. Moroz*, Tokyo Electron US Holdings

Theoretical and experimental understanding of plasma interactions with solid materials has led to development of 2D and 3D feature profile simulators. Different approaches have been used for over 40 past years for that. Our simulator, FPS3D [1-2], is a general code which uses a cellular model for representing solid materials and uses Monte Carlo pseudo-particles for representing all incoming fluxes of reactive species. Those particles are launched such that statistically they represent the angle-energy distribution of fluxes coming to the wafer from the plasma. Each particle typically contains many molecules, but preferentially significantly less than the number of molecules in a full cell. FPS3D is very different in many ways from other feature profile simulators, most importantly in the way how it represents gaseous and solid materials and how it represents interactions of reactive gaseous species with solids. The algorithms applied enable simulation of very large span of models ranging from large features of hundreds of microns to very small ones of a few nanometers where a cell size is approaching to the size of a single molecule. Regimes with application of beams, plasmas, or just reactive gases could be conveniently simulated. Interaction with solids is described very differently for low-energy and high-energy particles. While the low-energy gaseous species interact only with the surface layers of the cells, the energetic particles such as ions or fast neutrals could penetrate into the body of the cells, and could even go through the cells. The finite penetration depth of a fast particle into a solid material is a key factor dictating the regime of interaction. When an energetic particle moves through a cell, it loses energy there on collisions and bond breaking between atoms. The energetic particle finally stops and implants in a solid material. The deposited energy might be enough for

some molecules to diffuse to other cells or go through upper layers. This way, etching through polymer layers could be simulated. Correspondingly, FPS3D can simulate etching, deposition, and implantation processes going on at the same time. Also among new developments to be presented is the capability of considering multi-step (or multi-recipe) processes, when each step could have different fluxes to the surface and different chemistry. Another new development in FPS3D is a possibility of simulating pulsed-plasma effects. Examples are mainly based on a case of HARC etching of SiO₂ by the fluorocarbon-argon-oxygen plasma.

[1] P. Moroz, ECS Transactions, 35 (20) 25 (2011).

[2] P. Moroz, IEEE Transactions of Plasma Science, 39 (11) 2804 (2011).

11:40am **PS-ThM12 Feature Profile Evolution in Plasma Processing using On-Wafer Monitoring System**, *T. Kubota*, Tohoku University, Japan, *M. Sato*, Harada Corporation, Japan, *T. Iwasaki*, Mizuro Information & Research Institute, Inc., Japan, *K. Ono*, Mizuho Information & Research Institute, Inc., Japan, *S. Samukawa*, Tohoku University, Japan

Plasma etching is widely used for the fabrication of semiconductor devices and MEMS. However, irradiation damage and etching profile anomalies are severe problems for the plasma processes. We are developing a system to predict the etching profile and plasma irradiation damage by using a combination of the process monitoring on the sample stage of the plasma chamber (on-wafer monitoring) and a computer simulation, and are promoting the commercialization of this system [1]. We have already developed a sensor to measure the differential charge-up between the top and bottom of the high-aspect-ratio hole structure (on-wafer charge-up sensor) and have presented a concept of the charge-up simulation [2]. Here, we developed a calculation based on the on-wafer charge-up sensor measurement that enables for the fusion of the measurement and simulation.

The calculation was performed in two steps. First, a calculation is conducted to determine the situation in the sensor. Here, we developed a calculation to obtain the incidence condition of the ions and electrons from the measured value of the charge-up voltage. A high-speed algorithm (ICCG method) is used to obtain the electric field distribution because the calculation needs iteration to converge the charge-up voltage into the measured value. Second, subsequent calculations are conducted to obtain the charge-up voltage and ion trajectory of an arbitrary etching profile using the ion/electron incident condition obtained from the first calculation.

An on-wafer charge-up sensor with an aspect ratio of 10 was used for the plasma measurement. Then, the calculation was performed. As a result, it was predicted that etching is possible up to aspect ratio of 30, but the etching profile would be anomalous if the aspect ratio is more than 20.

This indicates that the etching profile of an arbitrary structure can be predicted based on a measurement and computer simulation.

[1] <http://www.mizuho-ir.co.jp/solution/research/semiconductor/fabmeister/onwafer/index.html> (in Japanese)

[2] H. Ohtake et al., Jpn. J. Appl. Phys. 49, 04DB14 (2010), B. Jinnai et al., J. Appl. Phys. 107, 043302 (2010)

Advanced Surface Engineering

Room: 203 C - Session SE+PS-ThM

Pulsed Plasmas in Surface Engineering (8:00-10:00 am)/Atmospheric Pressure Plasmas (10:40 am-12:00 pm)

Moderator: H. Barankova, Uppsala University, Sweden, J. Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada

8:00am **SE+PS-ThM1 A 60 Year Perspective on Developments in Plasma Assisted PVD Processes for Enhanced Surface Engineered Performance**, *A. Matthews*, University of Sheffield, UK **INVITED**

Over the past 60 years there have been many developments in PVD technology which have contributed to the successful emergence of the technological discipline which we now know as Surface Engineering. There now exist many products which could not even function without these developments, and other products whose performance so far-exceeds what was previously possible that they can offer improvements in measures such as productivity which are many hundreds (if not thousands) of times better than previously achievable. We can see these benefits in all major industrial sectors, especially aerospace, automotive, energy and healthcare. This paper highlights how these product enhancements have been achieved through a combination of plasma process developments and materials systems developments. The plasma processes have included ionisation enhancing

systems such as thermionic assistance, magnetic confinement and pulsed-plasmas, and the materials developments have included multi-layered and nanocomposite combinations of phases which have allowed the creation of surfaces with mechanical and chemical properties which were previously unachievable. We can now even create "duplex" engineered surfaces which combine plasma assisted diffusion treatments with optimised coatings, which allow the use of substrate materials (such as titanium and aluminium alloys) which were previously considered unsuitable for heavily-loaded tribological contacts in arduous conditions. The progress in process and performance enhancements is charted with examples from each decade over the past 60 years.

8:40am **SE+PS-ThM3 Optimized Magnetic Field Configuration for High Power Impulse Magnetron Sputtering**, *P. Raman*, *L. Meng*, *H. Yu*, *D.N. Ruzic*, University of Illinois at Urbana Champaign, *M. Schilling*, Dexter Magnetic Technologies, Inc, *S. Armstrong*, Kurt J. Lesker Company

Magnetic field design is critical in magnetron sputtering systems as it affects the plasma parameters and film quality. Most magnetic field configurations are designed for DC sputtering and they suffer from low target utilization, non-uniform ionized metal atoms, etc. High Power Pulsed Magnetron Sputtering (HIPIMS) discharge has high degree of ionization of the sputtered material with very high peak power on the target [1]. Therefore HIPIMS is an ideal candidate for the next generation magnetron sputtering systems. There are no magnetic field configurations that are optimized for HIPIMS discharge. It has been confirmed from our previous work on HIPIMS that a spiral-shaped magnetic field design on 36 cm diameter copper target was able to produce superior plasma uniformity on the substrate in addition to improved target utilization without the need for magnet rotation [2]. Commercial 4 inch sputter cathodes are very popular as they function with a wide variety of target materials and they can be operated with DC, RF and Pulsed-DC power supplies. These 4 inch cathode guns typically have a conventional circular magnetic field design (old). To optimize the magnet field configuration in HIPIMS for the 4 inch cathode gun, the spiral design (new) from the 36mm target was shrunk in size to produce the same magnetic field on the 4 inch target surface. In order to understand the effects of new magnet field configuration, the old and new magnet field configurations were tested in HIPIMS, Z-pulser and DC power supplies side by side using two 4 inch guns for deposition rate, film density, film uniformity and film stress. Plasmas from each power supply were diagnosed (ne, Te, ionization fraction) for the new and old magnet filed configuration in order to understand the pulsing parameters for better plasma control.

References

1. J. Bohlmark, J. Alami, C. Christou, A. P. Ehasarian and U. Helmersson, J. Vac. Sci. Technol. A, 23, 18 (2005).

2. He Yu, Liang Meng, Matthew M. Szott, Jake T. McLain, Tae S. Cho and David. N. Ruzic, Investigation and Optimization of Magnetic Field Configuration in High Power Impulse Magnetron Sputtering, Plasma Sources Sci. Technol (Submitted).

9:20am **SE+PS-ThM5 HiPIMS Deposition of Semiconducting ZnO Thin Films**, *A.N. Reed*, *P.J. Shamberger*, Air Force Research Laboratory, Wright Patterson Air Force Base, *C. Muratore*, University of Dayton, *J.E. Bultman*, University of Dayton Research Institute, *A.A. Voevodin*, Air Force Research Laboratory, Wright Patterson Air Force Base

High power impulse magnetron sputtering (HiPIMS) was demonstrated for the first time on semiconducting zinc oxide thin films for use as a transistor channel material. Nanocrystalline ZnO thin film transistors are of interest for integrated RF devices due to their high mobilities ($110 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and high on-off ratios (up to 10^{12}) [1]. These electrical transport properties are critically dependent on film microstructure, defect densities, crystal orientation, surface roughness and grain size. Due to a highly ionized flux, HiPIMS allows for control of thin film microstructure, while simultaneously producing high quality crystalline films on unheated substrates. However the use of HiPIMS for the growth of oxide semiconductors and their resulting electrical transport properties remain largely unexplored.

In this study, we investigate the interrelationship between the plasma characteristics, resulting film microstructure, and the electrical transport properties of nanocrystalline ZnO thin films. HiPIMS was used to deposit thin (~100 nm) ZnO films from ceramic ZnO and metallic Zn targets onto substrates heated to 150 °C. In both non-reactive and reactive cases, the resulting films had stronger crystallinity, more highly aligned (002) texture and lower surface roughness than films grown with pulsed DC sputtering, as determined by XRD, SEM and AFM measurements. The degree of alignment in the films was strongly dependent on the target potential, gas pressure and pulsing parameters. Film I-V characteristics were compared alongside microstructures to correlate electrical transport properties with specific aspects of microstructure (grain size, crystallinity, texture).

Similarly, time-resolved current measurements of the target and ion energy distributions, determined using energy resolved mass spectrometry, were correlated to film microstructure in order to investigate the effect of plasma conditions on film nucleation and growth. Finally, we will compare ZnO films grown by HiPIMS against those grown by other techniques (pulsed DC sputtering, pulsed laser deposition) and will critically evaluate the capability of HiPIMS for the deposition of electronic oxide films.

[1] B. Bayraktaroglu, K. Leedy, R. Neidhard. Microwave ZnO Thin Film Transistors. IEEE Electronic Device Letters V 29 Iss. 9, 1024-1026 2008

9:40am **SE+PS-ThM6 Si₃N₄ Spacers Etching in Synchronized Pulsed CH₃F/O₂/He/SiF₄ Plasmas**, **R. Blanc**, STMicroelectronics, France, **M. Darnon**, **G. Cunge**, **O. Joubert**, LTM – MINATEC – CEA/Leti, France

Gate spacers are used in submicron metal oxide semiconductor field effect transistor (MOSFET) in order to precisely define the channel length with abrupt junction geometry and eventually to tailor the electrical characteristics of the MOSFET transistors. Therefore, spacer etch process is considered to be one of the most critical processes of CMOS technologies. The Si₃N₄ spacer etching process requires a high etch selectivity to Si so that Si₃N₄ etching can be stopped on the Si surface without silicon substrate consumption in source/drain (S/D) regions of the MOSFET transistor. Silicon loss in S/D regions during spacer etching causes substrate bias dependent leakage and etch induced damage in the silicon surface raises the resistance of ultra-shallow junctions. More recently, the introduction of an ultra-thin Si channel in 28 nm FDSOI technology brought more aggressive requirements in terms of Si consumption. At the same time, plasma etch processes are reaching their limits regarding etch selectivity and profile control at the nanometer scale. In this study, we investigate the combination of synchronized pulsed plasma technologies and the addition of a Si-containing gas, SiF₄, with the objective to improve spacer etch process performance.

The experiments are performed in a 300mm AdvantEdge™ etch tool from Applied Materials. The inductively coupled plasma is sustained by two RF generators (13.56 MHz) to create the plasma and to polarize the wafer, using synchronous pulsing at different frequencies and duty cycles. Moreover, a Theta300 angle resolved XPS system from Thermo Scientific is connected under vacuum, allowing quasi in-situ analysis of etched samples.

In this work, we investigate the effect of SiF₄ addition in a synchronized pulsed CH₃F/O₂/He plasma. In a previous study, we have already shown that high Si₃N₄/Si selectivity is obtained by oxidizing the silicon surface during the landing of the nitride etching process on the silicon surface. When the plasma is pulsed at 1 kHz with a duty cycle of 10%, spacer profiles are improved and the oxidized thickness is significantly reduced but still generates a Silicon recess of 0.5 nm. With 5sccm SiF₄ added to the plasma gas phase, we observe a SiO_x deposition at the Si surface without any Si consumption, showing that the etch stop is obtained by the deposition of a SiO_x layer originated from the plasma gas phase.

10:40am **SE+PS-ThM9 CO₂ Conversion to CO and O₂ by DBD Plasma at Atmospheric Pressure**, **G. Arnoult**, **T. Bierber**, **A. Ozkan**, **P. De Keyser**, **F.A.B. Reniers**, Université Libre de Bruxelles, Belgium

Because of its high thermodynamical stability, carbon dioxide is usually considered as a waste, unavoidable end-product of many industrial processes. It is therefore necessary to develop technologies able to reuse it. In this objective, dry reforming of carbon dioxide by plasma has attracted significant interest to generate carbon monoxide which has an interesting energetic value [1],[2].

We present here a study of the plasma assisted conversion of CO₂ into CO and O₂ in a Dielectric Barrier Discharge plasma device operating at atmospheric pressure. We focus on determining the influence of several parameters on the conversion efficiency: the input power, the flow rate and finally the use or not of an additional plasmagen gas (argon or helium) in the mixture. Gas chromatography and mass spectrometry at atmospheric pressure are used to determine the composition of the gas after plasma treatment. Conversion rates for CO₂ can then be extracted.

The conversion rate increases with the power, suggesting an effect of the electron density (Fig.1 and Fig.2). On the other hand, the conversion rate drops with increasing flow rate from 0.1 L/min to 10 L/min. Indeed since the flow rate is inversely proportional to the residence time of the gas in the reactor, increasing it means that the gas spends less time in the plasma. Furthermore the addition of a plasmagen gas increases the conversion rate.

Optical emission spectroscopy and electrical measurements are also performed in order to have a better comprehension of the physical and chemical processes leading to the observed results.

[1] R. Li, Q. Tang, S. Yin, et T. Sato, « Plasma catalysis for CO₂ decomposition by using different dielectric materials », *Fuel Processing Technology*, vol. 87, n° 7, p. 617–622, 2006.

[2] S. Paulussen, B. Verheyde, X. Tu, C. De Bie, T. Martens, D. Petrovic, A. Bogaerts, et B. Sels, « Conversion of carbon dioxide to value-added chemicals in atmospheric pressure dielectric barrier discharges », *Plasma Sources Science and Technology*, vol. 19, p. 034015, 2010.

11:00am **SE+PS-ThM10 Cold Atmospheric Plasma Assisted Production of Hydrogen**, **L. Bardos**, **H. Baránková**, Uppsala University, Sweden

Experimental study of submerged cold atmospheric plasma generated in water and in water-based mixtures has been carried out. A hermetic stainless steel reactor with an originally designed coaxial plasma source immersed in the tested liquid has been used both with and without additional gas transported into the plasma zone. The reactor has been equipped with a pH meter, conductivity meter, thermometer, a simple pressure gauge, and a quartz fiber optics for optical emission spectroscopy of the submerged plasma. A sensor measuring the hydrogen content has been installed at the outlet of the reactor after rotameter tube measuring the outlet gas flow. The gas outlet has been provided also by a simple jet for gas flammability tests. Several types of the power generators have been tested for ignition and maintenance of the submerged plasma in the water and in water mixtures with ethanol. Preliminary experiments have confirmed production of the hydrogen containing synthesis gas that can be enhanced by adding ethanol admixtures. Very short dc pulses with average power of less than 50 W led to spontaneous formation of gas bubbles and flammable outlet gas with more than 50 % H₂.

11:20am **SE+PS-ThM11 Optical Emission Spectroscopy of He Dielectric Barrier Discharges at Atmospheric-Pressure Applied to the Functionalization of Wood Surfaces**, **L. Stafford**, **R.K. Gangwar**, **O. Levasseur**, Université de Montreal, Canada, **N. Gherardi**, CNRS-LAPLACE, France, **N. Naudé**, Université Paul-Sabatier, France

Application of dielectric barrier discharges (DBD) to the modification of “novel” materials such as nanostructured polymers is much more challenging than for conventional substrates such as Si or SiO₂. This can be attributed not only to the highly anisotropic nature of this polymer which can introduce spatial inhomogeneities of the electric field near the substrate surface, but also to its highly porous microstructure which can release impurities either from plasma-substrate chemical reactions or from sample outgassing. In this work, a porous wood sample (sugar maple, acer saccharum) was placed on the bottom electrode of a DBD operated in nominally pure helium to examine the influence of plasma-wood interactions and substrate outgassing on the evolution of the plasma properties. Optical emission spectroscopy revealed strong emission from N₂, N₂⁺, O and OH impurities. While the nitrogen and oxygen emission can be attributed to air outgassing, the OH emission was ascribed to etching of the weak boundary layer and humidity desorption from wood. We have calculated various line ratios from the time-resolved optical emission spectra. The He-588 nm-to-He-707 nm line ratio, 1588/707, was found to decrease from when going from right after ignition of the first few discharges where substrate outgassing is important to longer treatment times where “pumping” of the wood samples is nearly complete. Assuming that the He 3D and 3S levels (L•S coupling) giving rise to the emission at 588 and 707 nm are populated by stepwise excitation through the most populated metastable He 3S1 level and are lost by spontaneous emission, the 1588/707 line ratio becomes link to the ratio of the rate for stepwise excitation of the He 3D and 3S levels, which is only a function of the electron temperature T_e. Accounting for collisional energy transfer reactions between the He 3D, 3P, and 3S states in atmospheric-pressure plasmas and using the set of cross sections reported in literature for stepwise excitation, energy transfer reactions, and collisional quenching, it was found that the observed decrease of 1588/707 can be ascribed to a decrease of the electron temperature. Further analysis of the time evolution of the emission spectra and of the current-voltage characteristics indicated that the release of products from the wood substrate also yields to a significant quenching of He metastables. This method was further used to examine the detailed influence of hexamethyldisiloxane (HMDSO) and titanium isopropoxide (TTIP) injection on the plasma characteristics during plasma enhanced chemical vapor deposition of functional, nanostructured coatings on wood.

11:40am **SE+PS-ThM12 Substitution of ThO₂ by La₂O₃ for Tungsten Electrodes used in Atmospheric Plasma Spraying**, **M. Heissl**, **C. Mitterer**, Montanuniversitaet Leoben, Austria, **T. Granzer**, **J. Schroeder**, **M. Kathrein**, PLANSEE Composite Materials GmbH, Germany

ThO₂ additions are commonly used in tungsten-based electrodes for plasma spraying due to the excellent electron emissivity, improved arcing behavior, higher strength, and better machinability. Because of their radioactive potential, which makes handling, use, recycling, and disposal more difficult, alternative additives are required that provide the same advantages as thoriated tungsten, but without environmental hazards. Within this work,

tungsten cathodes with 2 wt.% ThO₂ and 1 wt.% La₂O₃ were compared with respect to their arc ignition behavior, plasma stability and arc erosion. Both, cyclic and continuous plasma spraying experiments were carried out. In addition, structure and mechanical properties of Al₂O₃ coatings sprayed on Mo substrates were evaluated. La₂O₃ is characterized by a similar plasma ignition and operation behavior as well as a comparable coating quality with respect to ThO₂ additions. Further, La₂O₃ additions caused a reduced degradation of the cathode material, which is attributed to the lower cathode temperature, giving rise to an expected longer lifetime.

Thin Film

Room: 102 C - Session TF+PS-ThM

Advanced CVD Methods

Moderator: R.C. Davis, Brigham Young University

8:00am **TF+PS-ThM1 Non-destructive Spectroscopic Analysis of Gradient Hydrocarbon/Fluorocarbon Thin Films to Demonstrate the Formation of a Stable Gradient Structure during PECVD Film Growth**, *B.D. Tompkins, E.R. Fisher*, Colorado State University

Thin films that have a continuous change in composition in one or more dimensions have a wide variety of potential applications, including biomimetic materials, barrier films, adhesion interlayers, and optical coatings. These gradient film structures are valuable for their ability to direct processes within a film or along a surface; the ability to tailor these materials allows for unprecedented control over such a process. We have developed a plasma enhanced chemical vapor deposition (PECVD) system capable of fabricating a range of arbitrary gradient film structures using dynamic mixing of C₃F₈ and H₂. We used time resolved optical emission spectroscopy (TR-OES) to characterize the PECVD process and found that the relative gas-phase density of key radical species change reproducibly based on the C₃F₈/H₂ ratio at any given time. Although the C₃F₈/H₂ composition can be varied continuously, verifying that a stable continuous gradient composition has been fabricated presents a more complicated analysis problem. Recently, we have adapted standard non-destructive spectroscopic analysis techniques to elucidate the structure within a gradient film. A series of homogenous films and model gradient films were examined using x-ray photoelectron spectroscopy (XPS), variable angle spectroscopic ellipsometry (VASE), and infrared spectroscopy (FTIR). By examining the shift in CF₂ binding energy from XPS, dielectric constant from VASE, and the shift in ν(CF₂) from FTIR, we demonstrate that stable confined layers with high fluorocarbon content remain incorporated into the gradient material when fabrication is complete. The ability to tailor surface composition and properties through programmed deposition will also be discussed.

8:20am **TF+PS-ThM2 CVD Infiltration of Carbon into Carbon Nanotube Forests for Templated Microfabrication**, *R.R. Vanfleet, W. Fazio, J.M. Lund, K. Zufelt, T. Wood, D.D. Allred, R.C. Davis, B.D. Jensen*, Brigham Young University

Chemical Vapor Deposition (CVD) of materials into patterned frameworks of carbon nanotube forests can be used to create precise high-aspect-ratio (up to 200:1) microstructures. We call this process carbon nanotube templated microfabrication (CNT-M). The "as grown" CNT forests are very low density (at 0.009 g/cc the forest is ~1% carbon and 99% air) and not useful as mechanical materials themselves because they are extremely fragile, due to their low density and weak intratube bonding. However, when we replace the air spaces between tubes in the forest with a filler material by atomistic deposition, the infiltrated CNT framework becomes a robust microstructure consisting mostly of the filler material. We have used various deposition techniques to infiltrate the CNT framework with a range of materials. This presentation will focus on the fabrication and characterization of structures using CVD of carbon into the nanotube forest. A range of characterization has been applied to the materials and resulting structures from high resolution electron microscopies of the base materials to bending and failure tests of full structures. The materials consist of nanocrystalline graphitic carbon coated on multiwalled carbon nanotubes. The complete structures exhibit fairly low Young's modulus (5-15 GPa), and ultimate strength (100-200 MPa) with a resulting high maximum strain of over 2%.

8:40am **TF+PS-ThM3 Initiated Chemical Vapor Deposition of Functional Polymers onto Porous Materials and Liquid Surfaces**, *M. Gupta*, University of Southern California **INVITED**

This talk will present the mechanism, kinetics, and potential applications associated with the vapor phase deposition of functional polymers onto structured materials and liquid surfaces. Vapor phase deposition eliminates

the need for organic solvents and thereby offers a safer and cleaner alternative to liquid phase polymer processing. We will demonstrate our ability to pattern functional polymers onto structured materials such as microfluidic devices, porous materials, and pillar arrays. We will also present our recent work demonstrating deposition onto liquids with negligible vapor pressures such as ionic liquids (ILs) and silicone oils. We will demonstrate that the polymer morphology at the liquid/vapor interface is controlled by surface tension interactions. The ability to controllably tailor polymer morphology at the interface allows for the design of ultrathin free-standing polymer films, micron-scaled particles, and core-shell particles. We will also demonstrate that polymerization can occur within the liquid layer allowing for the fabrication of polymer/IL composite films.

9:20am **TF+PS-ThM5 Ultrasonic Spray Deposition of Mesoporous WO₃ Films Displaying 100% Optical Modulation**, *C.-P. Li*, Colorado School of Mines, *C. Engrakul, R.C. Tenent*, National Renewable Energy Laboratory, *C.A. Wolden*, Colorado School of Mines

Smart windows employing electrochromic materials to reversibly modulate optical transmission and reflection can significantly improve building energy efficiency. However, further improvements in both performance and cost reduction are required for widespread implementation of electrochromic windows. Mesoporous films comprised of nanocrystalline domains can provide both high performance and good durability. Sol-gel chemistries combined with sacrificial templating agents is a well-established technique to introduce controlled porosity, but conventional techniques for film formation such as spin/dip coating are not amenable to large scale production. Ultrasonic spray deposition (USD) is an attractive technique for large scale, low cost thin film manufacturing of nanostructured thin films. USD provides high materials utilization and the use of benign solvents enables deposition under ambient conditions. Piezoelectric nebulizer technology addresses the quality and uniformity issues that were a concern with conventional pressure driven sprays. In this work mesoporous WO₃ films were deposited by adapting sol-gel chemistry to ultrasonic spray deposition. The sol was formed by dissolving WCl₆ and an organic templating agent (P123) in ethanol. The dynamics of both sol preparation and hydrolysis were investigated by UV-Vis spectroscopy. Electrochromic performance is strongly correlated to both the annealing conditions and the sol composition. Optimized films produced world record coloration efficiency (68 cm²/C), resulting in never before achieved 100% optical modulation across the visible spectrum during cycling. The films also displayed good switching kinetics, producing a 75% change in absolute transmission in 4 and 19 s during coloration and bleaching, respectively. Achievement of optimum electrochromic performance could be achieved by controlling the sol concentration and/or the number of spray passes in this robust process. The films were smooth and uniform, and the excellent performance is attributed to the nanocrystalline nature of the films, which provides high specific surface area (>100 m²/g) for efficient lithium ion intercalation.

9:40am **TF+PS-ThM6 Preparation and Characterization of CVD & ALD Tungsten & Molybdenum Thin Films for CNT-M Metallic Microstructures**, *D.D. Allred, R.R. Vanfleet, J.K. Anderson, C. Brown, R.S. Hansen*, Brigham Young University, *D. McKenna*, University of Notre Dame, *R.C. Davis*, Brigham Young University

Microelectromechanical systems (MEMS) fabrication traditionally uses the same limited methods and materials as those used in the silicon-based microelectronics industry. In order to make MEMS out of a much richer suite of materials, such as metals, Brigham Young University researchers are investigating chemical vapor infiltration and atomic layer infiltration of patterned carbon nanotube (CNT) forests, using the surface of the carbon nanotubes as nucleation sites for the metal deposition. Our goal has been to fill in the spaces between CNTs by atomistic deposition, thus creating a CNT-composite material possessing the original pattern of the CNT forest. We have investigated two 2 metals: tungsten and molybdenum and 3 precursors: tungsten carbonyl, molybdenum carbonyl and tungsten hexafluoride with hydrogen. molybdenum carbonyl proved to be more successful than tungsten carbonyl for infiltration. As deposited the materials are not pure metals, but contain substantial amounts of carbon and oxygen. As deposited the materials are not pure metals, but contain substantial amounts of carbon and oxygen. Efforts to remove impurities as well as the electrical and mechanical properties of the resulting composite material will be reported. Most recently tungsten fluoride via both CVI and ALI has been used to deposit purer tungsten structures.

10:40am **TF+PS-ThM9 Silica Structures by Plasma-enhanced Chemical Vapor Infiltration of a Carbon Nanotube Template**, *J.M. Lund, B.D. Jensen, R.C. Davis, R.R. Vanfleet*, Brigham Young University

This work investigates the advantages of infiltrating carbon nanotube structures with silica by plasma-enhanced chemical vapor deposition (PECVD). Carbon nanotube (CNT) forests have unique porous structures

created through CNT interaction during the growth process. It is possible to coat individual nanotubes with silicon oxide using a PECVD process. Oxidation of the carbon nanotubes then removes the initial CNT template, resulting in a uniquely structured silica material. One application of this work is the fabrication of ultra-low thermal conductivity films. Measurements indicate a thermal conductivity less than 0.05 W/m-K. However, with this particular process the coating is invariably thicker near the top surface and the silica typically penetrates no more than 17 μm into the CNT forest. The current challenge in this work is to keep the structures as porous as possible while coating enough at the base to keep the structure continuous and attached to the substrate. Some investigation is made into the parameters influencing, and possible uses of, the infiltration depth. This includes the usefulness in capping or sealing porous structures so they can be planarized in preparation for other films and structures.

11:00am **TF+PS-ThM10 High Deposition Rate and Uniformity of Silicon Thin Films Deposited Via Efficient, Low-Damage Surface Wave Plasma Source**, *J. Peck, P.S. Zonooz, D. Curreli*, University of Illinois at Urbana Champaign, *M. Reilly, R. Stubbers, B. Jurczyk*, Starfire Industries, LLC, *D.N. Ruzic*, University of Illinois at Urbana Champaign

An innovative surface wave plasma source provided by Starfire Industries, LLC has been tested by the Center for Plasma-Material Interactions at the University of Illinois Urbana-Champaign. Operating in the microwave range, the source efficiently generates high-density ($10^{11-12} \text{ cm}^{-3}$) and low electron temperature ($\sim 1 \text{ eV}$) plasmas. Thin silicon films were deposited with the interest of characterizing a cost-effective PECVD process for high quality silicon photovoltaics. Parameters of interest included substrate temperature, total operating pressure, silane dilution, RF power, discharge gap width, and process gas flowrate. Through a $\text{SiH}_4:\text{H}_2$ discharge, films were deposited and subsequently analyzed via profilometry, SEM, Raman microscopy, and X-ray diffraction. For a 15 cm source, consistent radial uniformity was maintained across a 12 cm diameter from $2.0 \pm 0.4 \text{ nm/s}$ up to $3.5 \pm 0.9 \text{ nm/s}$ at a 2.5 cm discharge gap. Well-formed films were produced with substrate temperatures above 285C. With decreasing operating pressure and increasing flowrate, area of coverage is shown to increase without compromising speed of film growth. An assessment on deposition rate optimization, film uniformity, and large-area scalability is presented.

11:20am **TF+PS-ThM11 Ab-initio and Classical Molecular Dynamics Study of Diffusion of Ti and N Adatoms on the TiN(001) Surface**, *D.G. Sangiovanni, D. Edström, L. Hultman*, Linköping University, Sweden, *I.G. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign, *V. Chirita*, Linköping University, Sweden

We carry out *ab-initio* and classical molecular dynamics (MD) simulations to investigate fundamental atomistic processes and surface properties responsible for TiN surface evolution during thin film growth. We find that Ti adatoms are highly mobile on TiN(001) terraces where they diffuse between fourfold hollow sites primarily via $\langle 100 \rangle$ channels. $\langle 110 \rangle$ diffusion via atop N terrace atoms, double and triple $\langle 100 \rangle$ jumps are also observed, and their occurrence is a function of TiN(001) temperature. When placed on TiN/TiN(001) islands, Ti adatoms funnel toward cluster edges and corners, where they rapidly descend by either direct hopping or push/out-exchange. Ti and N adatoms diffusion on square islands is anisotropic and results in preferential channels for mass transport. N adatoms, considerably less mobile than Ti adatoms, can form strong chemical bonds with underlying terrace or island N atoms. As an effect of this bonding, N adatoms can diffuse on TiN(001) terraces by exchange with N terrace atoms. At high temperatures, the rapid lattice vibrations assist the desorption of N_2 (N-adatom/N-terrace) dimers, and anion vacant sites are produced in the TiN(001) terrace. When placed on square TiN/TiN(001) clusters, N adatoms can pull Ti corner atoms onto the island to form TiN dimers which descend via direct hop over the island edge. Both N and Ti adatoms slowly diffuse along island edges. In contrast, due to the high degree of ionicity in Ti-N bonds, Ti and N adatoms easily diffuse around island corners of the same chemical type via 1D push-out/exchange due to electrostatic repulsion. Corners of opposite chemical type are rapidly rounded by direct diffusion. Finally, we combine the Arrhenius plots obtained from classical, and quantum-mechanical simulations to determine, with high accuracy, Ti and N adatom diffusion energy barriers and diffusion coefficients on TiN(001). The excellent agreement between empirical and *ab-initio* methods results further demonstrates the ability of classical interaction potentials for accurate, fully-deterministic, simulations of thin films deposition.

11:40am **TF+PS-ThM12 Quantum Chemistry Analysis of the Role of Radicals in Plasma Assisted Atomic Layer Deposition of Silicon Nitride Films**, *J. Yoshikawa, N. Fukiage, S.Y. Kang*, Tokyo Electron Ltd., *P. Ventzek*, Tokyo Electron America, *H. Ueda*, Tokyo Electron Ltd.

Silicon nitride films are well known as important dielectric components for semiconductor device fabrication because of their good physical and electrical properties for 3D structure device construction. High quality silicon nitride film deposition has been demonstrated in high density plasma sources by using RLSA™ in which a nitrogen and hydrogen containing plasma nitrates a silicon surface deposited by a thermal adsorption process. [1] A typical precursor for the silicon component is Dichlorosilane (DCS), used in thermal CVD of silicon nitride. [2] In plasma assisted atomic layer deposition of silicon nitride films, silicon nitride deposition is effected by alternating deposition and nitridation steps. The film quality, defined by the 0.5% DHF solvent wet chemical etching ratio, is a function of many process parameters. It has been shown experimentally that hydrogen radicals produced in this plasma are important for film quality. The exact film growth mechanism in plasma assisted deposition processes is, as yet, not fully clarified and most studies are related to thermal CVD. *Ab-initio* studies focusing on the role of radicals are rare. In this presentation a quantum chemistry analysis (Gaussian 09) of the film formation mechanism in Atomic layer Deposition sequence is presented. Hexachlorodisilane (HCD) is used as a model surface in the study. We revealed the role of H as a critical precursor for the growth of high quality films. Un-dissociated ammonia or hydrogen interacts with Si-Cl to liberate chlorine from silicon. Hydrogen liberates H from the new NH_2 structure. Silicon containing structures with dangling bonds interact with the structure then complete the formation of Si-N-Si bonding. Hydrogen and NH_x limit restoration of the Si-Si chain.

[1] T. Karakawa, M. Oka, N. Fukiage, H. Ueda, T. Nozawa, PS+TF-ThM1 AVS Symposium Nashville (2011) [2] A. A. Bagatur'yants, K. P. Novoselov, A. A. Safonov, L. L. Savchenko, J. V. Cole and A. A. Korokin, Materials Science in Semiconductor Processing 23, 3 (2000)

Thursday Afternoon, October 31, 2013

Graphene and Other 2D Materials Focus Topic

Room: 104 B - Session GR+AS+BI+PS+SS-ThA

Plasma Processing, Surface Chemistry, Functionalization, and Sensor Applications of 2D Materials

Moderator: P.E. Sheehan, Naval Research Laboratory

2:00pm **GR+AS+BI+PS+SS-ThA1 Carbon Monoxide-induced Reduction and Healing of Graphene Oxide, S.L. Weeks, B. Narayanan, B.N. Jariwala, Colorado School of Mines, B. Macco, J.W. Weber, Eindhoven University of Technology, Netherlands, M.C.M. van de Sanden, Eindhoven University of Technology; DIFFER, Netherlands, C.V. Ciobanu, S. Agarwal, Colorado School of Mines**

Reduction of graphene oxide (GO) has recently generated intense research interest due to the possibility of using this method to inexpensively produce large quantities of graphene. Current reductive processes rely on thermal or chemical removal of oxygen functional groups from the surface. While reduction has been demonstrated, a certain fraction of residual oxygen remains after processing with current techniques. Furthermore, the use of high process temperatures in the reduction of GO leads to the generation of defects through the loss of carbon atoms from the basal plane of graphene. The ultimate improvement in the electronic, optical, or mechanical properties of graphene that can be achieved through reduction of GO is limited by defect formation and the residual oxygen remaining after reduction through present reported methods. Here, we report the facile removal of oxygen functional groups from the surface of GO through reduction in a carbon monoxide atmosphere. Common oxygen-containing functional groups on the basal plane of GO (epoxides, hydroxyls, and ketone pairs) are removed from the surface due to the reducing action of CO. First, we have used molecular dynamics simulations and density functional theory calculations to elucidate the mechanisms of removal of these surface species by CO, and show that this reduction process proceeds without degradation of the underlying graphene sheet; CO₂ and H₂O are the only surface reaction products. We also show that the corresponding activation energy barriers for these reactions are easily surmounted at low temperatures. Second, the removal of oxygen-containing functional groups from GO by CO is confirmed experimentally using *in situ* attenuated total reflection Fourier transform infrared spectroscopy, indicating the reduction of the GO surface with CO is consistent with our atomistic-level calculations. Third, through controlled generation of defects into an otherwise pristine graphene sheet, we show that exposure to CO results in near-complete healing of the sheet as demonstrated with *ex situ* Raman spectroscopy. Thus, our results indicate CO induced reduction of GO not only proceeds without damaging the underlying sheet, but also heals defects that are produced in the production of GO via exfoliation of oxidized graphite.

2:20pm **GR+AS+BI+PS+SS-ThA2 Plasma Enhanced ALD of Hafnium Oxide on Graphene Layer with Plasma Pretreatment, T. Kitajima, T. Nakano, National Defense Academy of Japan**

Graphene is the candidate of the future generation semiconductor material due to its high mobility of electrons and ultimately thin feature of the 2D structure. The use of graphene for CMOS technology to replace current silicon devices requires matching of each interface between the substrate, electrodes, channel, and dielectrics. Among these, growth of high dielectric constant film growth over graphene is not successful due to the chemically inert nature of the graphene surface. In order to have reactive chemical bond on graphene surface, there are trials of oxidation with ozone, etc.

Here, the effect of the oxygen plasma pretreatment on the graphene surface is examined in this study.

Graphene layer is prepared by peeling method from HOPG using adhesive tape. The domain size is 1 micron in width. (AFM topograph is shown in Fig. 1) The pretreatment of the graphene surface is the exposure of O₂ ICP at 30 Pa for less than 1 min. This atomically modifies the topography (fig. 2), and the chemistry of the surface (fig. 3). The XPS analysis indicates the many of the graphene 2D bonds are replaced by C-O or C-OH bond and the defects are increased.

The growth sequence of Hafnium oxide ALD consists of the exposure of metal precursor (Tetrakis Ethyl Methyl Amino Hafnium : TEMAH) with N₂ buffer flow, N₂ purge, and O₂ ICP at 30 Pa.

The chemical composition from XPS shows the film thickness is specifically controlled by ALD cycle number and it saturates at 4th cycle owing to the limited mean free path of photoelectrons.

The initial growth stage of the film with and without plasma pretreatment is compared for 2nd ALD cycle sample. (AFM in fig. 4 and 5). With pretreatment, the surface consists of 2-5 nm width dispersed nano-islands and 20 nm width HfO₂ mesa (film) of 1nm height. Mesas are separated by base graphene surface by 10 nm pitch. Without pretreatment, the surface is covered by closely packed 5-10nm width nano-islands, around 1nm of height. This comparison indicates the oxygen bonds introduced by O₂ plasma pretreatment contribute to the chemisorption of the precursor and successful 2D growth of HfO₂ in the initial stage. In contrast, inert graphene surface without pretreatment prohibits the interconnection of the physisorbed precursor with the surface and 3D island growth is preferred.

In summary, although the domain size of the HfO₂ is limited to around 20 nm, 2D mode growth is enabled by the introduction of O₂ plasma pretreatment. Further progress is necessary on the increase of the coverage of the film, minimizing the oxidation of the base graphene layer, and reducing nano-sized islands on the film.

2:40pm **GR+AS+BI+PS+SS-ThA3 Detection of Uranium and Plutonium by Graphene-Based Nanosensors, G. Sandi, Argonne National Laboratory, A. Bobadilla, Texas A&M University, A.V. Sumant, L. Ocola, Argonne National Laboratory, J. Seminario, Texas A&M University, C. Mertz, M. Kaminski, Argonne National Laboratory**

The design and fabrication of arrays of electronic molecular devices as sensors for plutonium and uranium at the nanoliter volume will be discussed. Computational calculations performed at Texas A&M University and experiments performed at Argonne National Laboratory (Center for Nanoscale Materials and Chemical Sciences and Engineering Division), will be presented. In particular, we are studying graphene, which is a vibronic, plasmonic, and electronic material for molecular circuits and sensors. The idea is to use the plasmonic features of graphene molecules in order to transfer the electrical, magnetic, vibrational, and optical characteristics of nuclear agents into the graphene plasmon, which produces an enhancement (amplification) of observable quantities as successfully done with chemical and biological agents. For nuclear agents, we have additional possibilities due to their radiation features. Theoretical simulations have shown the possible use for sensors to identify single molecules with high selectivity and sensitivity that will contribute to the miniaturization, as well as efficient transport and processing of signals using graphene based devices. It is expected that this approach will allow us not only to sense targeted agents, but also to perform chemical recognition using molecular potentials, which have become the signature at the nanoscale, perfectly suitable for detection and identification of atoms and small molecules. Maps of the molecular potentials around complexes of U and Pu allows us to distinguish their main signatures similar to those observed in biological systems where receptors are able to distinguish to its transmitters or when a donor of electrons is able to match with an acceptor. The information obtained, especially following a supercritical nuclear event, would severely limit the list of potential actors and provide critical information to guide a proper and timely response.

Acknowledgments

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3:00pm **GR+AS+BI+PS+SS-ThA4 Damage-free Etching of Graphene using Oxygen Neutral Beam towards Edge State Control, T. Okada, K. Igarashi, S. Samukawa, Tohoku University, Japan**

The band gap of graphene needs to be controlled for electronic device applications because it is a zero band gap semiconductor. Narrow width graphene, which is called graphene nanoribbon (GNR), has an effective band gap and solves several problems. Although there are several approaches to fabricating GNRs, top-down lithographic patterning is the most attractive method for the well-arranged GNRs required for large-scale device integration. However, conventional plasma etching always produces high density defects around the edges of the GNRs due to UV irradiation. This makes it difficult to obtain a sufficiently large band gap and the high mobility necessary for GNR-based FETs using wide GNRs (>10 nm). We developed an etching process using a damage-free neutral beam (NB) to

fabricate the GNRs that can eliminate the UV irradiation to overcome this issue. We compared oxygen neutral beam etching to oxygen plasma etching within the same flux and energy conditions to clarify the defect generation mechanism at the edges of graphene.

Graphene sheets were extracted by micromechanical cleaving them from the HOPG and depositing them onto the substrate. The graphene was then etched using a stencil mask. The laser spot for taking the Raman measurement was shifted step by step to measure the defects at the edges. The Raman peaks at approximately the D-band and G-band were examined.

At the edges, the D/G ratio was increased, indicating that the defects were not generated on the plane but on the edge of the graphene. We also found that the D/G ratio on the edge etched by using oxygen NB was extremely lower than that for plasma. These results suggest that high-quality graphene edges can be easily fabricated using NB etching. The defects on the edges from the plasma etching were caused by UV radiation. Several studies have reported this defect generation on materials by high-energy UV photons during the plasma processing. Since UV photons have a non-orientation, they irradiated to the edges during etching. In contrast, in the case of neutral beam etching, damage-free etching was possible because the UV radiation was suppressed.

We concluded that NB etching is a promising candidate for GNR fabrication for high-mobility graphene transistors. In addition, this damage-less etching technique can be used for defect free formation of graphene nano structures, like nano dots and its periodic array when using the top-down process.

3:40pm **GR+AS+BI+PS+SS-ThA6 Controlling the Chemistry of Graphene.** *S. Hernández, E.H. Lock, Naval Research Laboratory, C. Bennett, Nova Research, C. Junkermeier, F. Bezares, S. Tsoi, Naval Research Laboratory, R. Stine, Nova Research, J.T. Robinson, J. Caldwell, T. Reinecke, P.E. Sheehan, C.R. Tamanaha, S.G. Walton, Naval Research Laboratory*

Graphene has attracted widespread interest because of its unique structural and electronic properties. Given its pure two dimensional nature, adsorbates have a strong impact on these properties and so global chemical modification provides opportunities towards homogeneous control of graphene films. However, control over the spatial distribution of chemical moieties provides an even greater functionality in that the properties can be manipulated locally, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Global and spatial chemical functionalization of graphene using electron beam generated plasmas will be discussed. The resulting chemical, structural, and electrical properties of the functionalized graphene as they originate for -oxygen, -fluorine, and -nitrogen functionalities will be demonstrated. This work is supported by the Naval Research Laboratory Base Program.

4:00pm **GR+AS+BI+PS+SS-ThA7 Covalent Functionalization of Graphene with Fluorine by Plasma Treatment.** *G. Mordí, S. Jandhyala, S. McDonnell, R.M. Wallace, J. Kim, The University of Texas at Dallas*

As the performance of graphene based devices has continued to improve over the years (mobility, contact resistance, transconductance), the realization of novel logic devices as the BiSFET (Bi-layer Pseudospin Field-Effect Transistor) for ultra-fast switching speeds and ultra-low power consumptions may not be far off. One of the challenges in realizing BiSFET¹ is the integration of a thin (1-2 nm), low-k (~2) dielectric material which can electrically isolate the two graphene layers in which a condensate is formed and at the same time act as a tunnel barrier.

One approach for obtaining a low-k dielectric is using two dimensional materials similar to graphene which can be manufactured independently and transferred on top of graphene. Covalent functionalization of graphene is a process of adding functional groups which covalently bind to the graphene network, changing its structure from sp^2 to sp^3 hybridization resulting in opening of a band gap. Fluorination among other processes (graphene oxide¹, graphane²) can be used to covalently functionalize graphene. Fluorinated graphene (GrF) is an interesting material because of its atomically thin nature, thermodynamically more stable compared to graphene oxide and graphane, has a wide band gap (~3-7.5 eV) and a potentially low-k dielectric (expected to have dielectric constant of ~2)².

In this study we utilized fluorine based plasma (CF₄) to covalently functionalize graphene films. We established suitable CF₄ plasma exposure parameters and then investigate the conduction mechanisms across GrF based devices. Raman spectroscopy studies showed the evolution of Raman active D (~1350 cm⁻¹), G (~1595 cm⁻¹), D' (1620 cm⁻¹) and 2D (~2680 cm⁻¹) peaks as function of plasma exposure (fluorination) time. XPS studies revealed the type of bonding that exists between fluorine and carbon atoms of the graphene lattice. Conductive atomic force microscopy (C-AFM) showed the *out-of-plane* conductivity on the GrF films were significantly

small compared to non-fluorinated films. *In-plane* transport characteristics of GFETs displayed two minima (or Dirac points) for short CF₄ exposures possibly attributed by both ionic and covalent doping effects simultaneously. Longer exposures result in a single minimum conductivity point possibly due to dominant covalent functionalization effects.

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4:20pm **GR+AS+BI+PS+SS-ThA8 Field Effect Control of Carrier Conduction in Helium Ion Irradiated Graphene.** *S. Nakaharai, T. Iijima, S. Ogawa, AIST, Japan, S.-L. Li, K. Tsukagoshi, NIMS, Japan, S. Sato, N. Yokoyama, AIST, Japan*

We demonstrate the gate control of carrier conduction in graphene which is functionalized by Helium ion beam irradiation in a Helium Ion Microscope (HIM) [1]. Carrier conduction control is important for graphene application to electronics, but it has long been an obstacle to realization of graphene electronics. We found that an appropriate amount of He ion dose to graphene induced point defects which enabled gate bias control of current with an on-off ratio of two orders of magnitude at room temperature.

Helium ions were applied to graphene with ion doses from 2.2×10^{15} ions/cm² to 1.3×10^{16} ions/cm². The induced defect density was estimated by numerical calculation to be 0.2% to 1.3% [2]. The introduction of defects was confirmed by the D-mode peak of Raman spectroscopy. A series of samples with different ion doses exhibited a drastic decay of current by more than five orders of magnitude as the defect density increased from 0.2% to 1.3%. In spite of such a drastic change in current, the basic structure of graphene remained, as evidenced by G-mode peak of the Raman spectra. Room temperature current switching with an on-off ratio of two orders of magnitude was realized at a moderate defect density of 0.9%. We also found that the current exhibited an exponential decay as the irradiated region length increased from 5 to 50 nm. These results suggest that the carriers in graphene are spatially localized due to interference of waves which are scattered at the randomly distributed defect sites. A theoretical investigation of localization in a defective graphene has predicted that 1% point defects will cause a strong localization of carriers [3], which shows good agreement with our experimental results. Therefore, it should be argued that the gate control of carrier conduction is realized by a transport gap which is generated by defect-induced localization.

Since the presented technique of graphene functionalization is a "top-down" process, it is easily introduced to the fabrication process of future electron devices. We will also present the application of our ion irradiation technique to the channel of graphene transistors [4] which achieved nearly four orders of magnitude on-off ratio at 250 K.

This research is granted by JSPS through FIRST Program initiated by CSTP.

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5:00pm **GR+AS+BI+PS+SS-ThA10 Epitaxial Graphene Oxide.** *E. Riedo, A. Bongiorno, Georgia Institute of Technology, Y.J. Chabal, University of Texas at Dallas, C. Berger, Georgia Institute of Technology, C. Aruta, CNR*

INVITED

Graphene and graphene-based materials hold great promise for the next generation of nanodevices. One of the most pressing issues for the technological use of graphene is the possibility to control physical and chemical properties by means of ad hoc functionalization. Thermal, chemical and optical reduction of graphene oxide have been explored as a route to produce graphene-based materials with the desired electron transport, mechanical and optical properties. Here, we demonstrate the ability to reduce graphene oxide at the nanoscale by using hot AFM tips (thermochemical nanolithography, TCNL). The resulting nanostructures have a conductivity that can be tune over 4 orders of magnitude [1]. Graphene oxide is indeed a material of great interest for its potential applications in nanoelectronics, nanoelectromechanical system, sensors, polymer composites, catalysis, energy storage devices and optics. However, the chemistry of graphene oxide and its response to external stimuli such as temperature and light are not well understood and only approximately controlled. This understanding is crucial to enable future applications of this material. We have carried over a combined experimental and density functional theory study [2] which shows that multilayer graphene oxide

produced by oxidizing epitaxial graphene through the Hummers method is a metastable material whose structure and chemistry evolve at room temperature with a characteristic relaxation time of about one month. At the quasi-equilibrium, graphene oxide reaches a nearly stable reduced O/C ratio, and exhibits a structure deprived of epoxide groups and enriched in hydroxyl groups. This study shows that the structural and chemical changes are driven by the availability of hydrogen in the oxidized graphitic sheets, which favors the reduction of epoxide groups and the formation of water molecules. Furthermore, we have discovered that a mild chemical oxidation of multilayer epitaxial graphene produces uniform oxidized films showing no propensity to exfoliate. XRD measurements show that the epitaxial graphene oxide films are extremely well ordered with an interlayer distance of 10 Å [3].

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Plasma Science and Technology

Room: 104 C - Session PS-ThA

Low Damage Processing

Moderator: E.V. Johnson, LPICM-CNRS, Ecole Polytechnique, France

2:00pm PS-ThA1 Damage Control: Electron Beam Generated Plasmas for Low T_c Processing. S.G. Walton, Naval Research Laboratory INVITED

The advantages of plasma-based materials processing techniques are numerous. The capability to modify large ($> 10^3 \text{ cm}^2$) areas with precision down to the nanoscale is one reason plasmas are widely used in the materials and surface engineering communities. However, with the rapidly evolving demand for new materials in applications ranging from organic and nanoelectronics to biosensors, some of the limitations of conventional plasma sources are becoming apparent. The lack of process control and excessive ion energies in the processing of soft or very thin materials are examples.

The Naval Research Laboratory (NRL) has developed a processing system based on an electron beam-generated plasma. Unlike conventional discharges produced by electric fields (DC, RF, microwave, etc.), ionization is driven by a high-energy ($\sim 2 \text{ keV}$) electron beam. This approach provides a solution to many of the problems associated with conventional plasma processing systems, making it potentially useful in the development of a wide variety of novel materials. Importantly, high plasma densities (10^{10} - 10^{11} cm^{-3}) can be produced in electron beam generated plasmas, while the electron temperature remains between 0.3 and 1.0 eV. Accordingly, ions leaving the plasma impact surfaces with energies in the range of 1 to 5 eV. This provides the ability to slowly etch and/or controllably engineer both the surface morphology and chemistry, critically important features for applications requiring atomically thin or smooth materials.

An overview of NRL's research efforts in developing this technology with a focus on source development, plasma characterizations, and materials processing will be presented. Particular attention will be given to current efforts in the processing of polymers and 2-d materials such as graphene, where we take advantage of the unique attributes of electron beam generated plasmas to engineer the surface properties of these materials for electronic and sensing applications. This work is supported by the Naval Research Laboratory base program.

2:40pm PS-ThA3 Numerical Simulation of Oxidation Process in Silicon by O₂ Gas Cluster Beam, K. Mizotani, M. Isobe, S. Hamaguchi, Osaka University, Japan

A surface modification process based on a gas cluster ion beam (GCIB) is known to be less damaging to the surface than that based on an ordinary atomic or molecular ion beam. In a GCIB process, several thousands of atoms or molecules aggregated by Van der Waals interactions form a gas cluster and such gas clusters are ionized and accelerated up to a high kinetic energy (typically in the range of several keV) toward a surface that is to be processed. Although the total acceleration energy for each cluster can be very high, each atom or molecule has relatively low kinetic energy. Therefore a GCIB process is essentially a low energy beam process. In this study, we use molecular dynamics (MD) computer simulations to examine

surface oxidation processes for silicon (Si) by oxygen-molecule GCIBs at various incident energies and compare the results with those of earlier experimental studies. Especially in this study, we focus on extremely low energy processes, where incident oxygen molecules in gas clusters have kinetic energies close to thermal energy at room temperature. It has been found in MD simulations that only the top surface layer of the substrate can be oxidized with little damage to the surface in GCIB processes. This is in contrast with oxygen molecular-ion beam processes, where oxygen hardly sticks to the Si surface when the beam kinetic energy is sufficiently low (so that the chemical bond of O₂ cannot be broken). If the kinetic energy is high, then the surface can be oxidized but the beam impact causes surface damage. It has been observed that, in the case of low-energy gas cluster beam incidence, each gas cluster sticks to the Si surface for dozens of picoseconds until the gas cluster is sublimed by heat transport from the substrate. While a cluster remains on the substrate surface, a large number of oxygen molecules with a solid density are directly exposed to the substrate surface, which increases the probability for the formation of Si-O bonds only on the top surface.

3:00pm PS-ThA4 Ultra-low k Dielectric and Plasma Damage Control for Advanced Technology Nodes (10-nm and Below), F. Lazzarino, IMEC, Belgium, M. Krishtab, KU Leuven, Belgium, S. Tahara, TEL, Belgium, M. Baklanov, IMEC, Belgium

The continuous decrease of the critical dimension together with the introduction of new porous low-k materials (k-value lower than 2.5) make plasma etch more and more challenging. Besides the morphological aspect (profile of the structure or bottom roughness), the degradation of the dielectric properties of the low-k film is another important point that needs to be understood and well-controlled. In this work, we compare and analyze the damage (loss of Si-CH₃ groups and moisture absorption) caused by different types of fluorocarbon-based chemistries and we propose a new damage-free chemistry to pattern advanced low-k materials identified for the most advanced technology nodes.

In the first part of the study, the low-k film is exposed to a selection of few conventional C₄F₈-based chemistries. In all cases, a significant level of damage is observed and is mainly attributed to the diffusion of fluorine radicals coming from the fluorocarbon polymer layer deposited on the low-k surface. As fluorine cannot be suppressed from the discharge, two options are considered to reduce its concentration in the passivation layer. First, a less polymerizing gas like CF₄ is used to replace C₄F₈ then a carbon-free molecule like NF₃ is considered to fully modify the nature of the passivation layer. Both approaches led to a very low level of damage. However, all CF₄-based chemistries show very low etch rate and exhibit a poor selectivity towards masking layers like TiN. In contrast, a much higher etch rate and a greater selectivity is observed when NF₃ is used to replace C₄F₈. Concerning the damage, an extremely thin ($\sim 1\text{-nm}$) but very hydrophilic carbon depleted layer is formed at the low-k surface and a rough surface appears while the etch front progresses. We characterized and understood these issues using FTIR spectroscopy, Auger analysis and AFM and we fixed both instabilities together by slightly adapting the chemistry. The optimized chemistry leads to a very low level of water absorption within an extremely thin and smooth damaged layer. Finally, a comparative study including k-value, surface roughness and composition of the damage layer using TOF-SIMS is presented applying our best C₄F₈-, CF₄- and NF₃-based chemistries on two potential low-k candidates for the 10-nm technology node.

To conclude, it is shown that a very low level of damage is obtained by using a C-free NF₃-based chemistry. The two side effects like the surface roughness and the high moisture uptake were characterized and the chemistry was tuned in order to overcome both issues. This new chemistry is rated as the best candidate to pattern ultra-low k dielectrics for the most advanced technology nodes.

3:40pm PS-ThA6 High Temperature Etching of GaN Preserving Smooth and Stoichiometric GaN Surface, R. Kometani, K. Ishikawa, K. Takeda, H. Kondo, M. Sekine, M. Hori, Nagoya University, Japan

Plasma etching of GaN is necessary for fabricating high performance GaN devices, however plasma exposure generates defects and produces residues, which results in degradation. It is strongly required that the damage induced by plasma etching should be reduced. Post annealing can recover damages, however, preferentially N lost causes Ga-rich surface. The stoichiometric surface was reported to be deteriorated under annealing of 200 to 1000°C after N₂⁺ sputtering at room temperature.¹ We have revisited the surface reactions at high temperature (HT).

We constructed a high-temperature plasma reactor,² where a CCP was generated by 13.56-MHz rf power to the substrate electrode. Ion bias energy was determined about 250 eV. SiC sample stage can be rapidly heated up to 800°C by an IR lamp as fast as 100°C/s.

As the GaN was exposed to Ar plasma at 600°C, a rough surface appeared with a root-mean-squared (RMS) value of 9.88 nm in AFM image. By XPS analysis of the shoulder peak at 18.9 eV in the Ga 3d region, it revealed Ga metallic state or Ga cluster formation. In contrast, no significant increase of roughness (1.46 nm) was observed after N₂ plasma exposure even at 600 °C.

On the other hand, for Cl₂ plasma, the etch rate increased at HT, from 293 to 534 nm/min for 300 to 600°C, and hexagonal pits were formed for 600°C etching. These mean that the heating would prompt the chemical reaction. The optical properties were investigated for YL (deep level defects such as N vacancy), BE (GaN band gap emission), and their ratio indicates crystal quality. Ar plasma exposure increased the YL/BE. It means crystal quality deterioration and deep level defects generation. The shallow level defects were also increased and not only YL but also lower energy side of BE increased. However, the crystal quality after Cl₂ plasma etching was much better than that of Ar plasma.

In Cl₂ plasma, no metallic gallium at any temperature, etch rate increasing and smooth surface was retained at HT except the hexagonal pits formation at 600°C. Consequently, HT etching is effective to enhance the surface chemical reaction and reducing plasma damages.

This work was supported by the Knowledge Cluster Initiative (Second Stage), MEXT, Japan.

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4:00pm PS-ThA7 Investigation of Surface Roughness in III-V Semiconductors After an *In Situ* Hydrogen Plasma Clean Prior to PEALD, E. Cleveland, NRL-ASEE, L. Ruppalt, B. Bennett, S.M. Prokes, NRL

III-V compound semiconductors, such as GaSb, are attracting widespread attention as an alternative to Si in advanced complementary metal-oxide-semiconductor (CMOS) technologies; their high electron and hole mobilities, as well as relatively narrow bandgaps, makes them particularly well-suited for high-speed, low power applications. However, for high-performance device realization, the quality of the interface between the III-V semiconductor and the gate-oxide is crucial. Most III-V semiconductors have a highly reactive surface and unlike SiO₂, the native oxides are complex in structure and composition leading to the formation of heavily defected interfaces that pin the semiconductor Fermi-level near midgap and degrades device performance. A significant effort has been focused on surface preparations prior to ALD that removes the native oxide and passivates the III-V atoms in order to ensure the best possible interface. Current approaches typically rely upon wet-chemical etches to remove the defect-prone native oxide layer prior to dielectric deposition; however, this technique typically suffers from a lack of reproducibility, as well as potential interface contamination between processing steps.

Recently, we demonstrated the use of an *in situ* hydrogen plasma treatment prior to the deposition of plasma enhanced ALD (PEALD) Al₂O₃ on GaSb. Samples demonstrating good electrical characteristics correlated to the elimination of Sb-oxide, a decrease in elemental Sb, as well as an increase in Ga₂O₃ as determined by XPS. While using plasma has been shown to produce good quality interfaces and subsequent dielectric films, a significant amount of surface roughening can take place across the semiconductor surface. Although surface roughness may not greatly influence the capacitance modulation of a MOS capacitor, it could significantly hamper charge mobility within a field-effect transistor (FET). Therefore, we investigated the surface roughness of a GaSb surface after exposure to hydrogen plasma as a function of select plasma parameters: rf-power, substrate temperature, and exposure time. Surfaces were characterized using atomic force microscopy, transmission electron microscopy, as well as, electrical measurements. Furthermore, we investigated the surface roughness across GaAs samples of different facets when exposed to a hydrogen plasma prior to PEALD in order to gain a better understanding of surface interactions during plasma assisted ALD.

4:20pm PS-ThA8 Fabrication of GaAs/AlGaAs Nano-Pillars using Bio-Template Combined with Neutral Beam Defect-Free Etching, C. Thomas, Y. Tamura, A. Higo, Tohoku University, Japan, N. Okamoto, I. Yamashita, Nara Institute of Science and Technology, Japan, S. Samukawa, Tohoku University, Japan

Quantum dot (QD) lasers have been extensively studied in the last few decades due to their device characteristics benefits. However, fabrication of a high density and uniform two-dimensional array of QDs is still a big challenge. We have developed the first damage-free top-down process for creating GaAs QDs by combining a high-density bio-template [1] and a neutral beam (NB) etching process [2]. The bio-template consists of a high-density (about 7x10¹¹ cm⁻²), two-dimensional array of cage-shaped proteins called ferritins with encapsulated metal oxide nanoparticles (NPs). After

removal of the protein shell, 7 nm in diameter iron (Fe) or cobalt (Co) oxide NPs were used as etching masks. The NB etching consists of an inductively coupled plasma chamber separated from the process chamber by a carbon electrode with a high-aspect-ratio aperture array. As a result, the charged particles are efficiently neutralized whereas almost no UV photons can reach the sample.

A thin oxide layer was deposited on top of the single quantum well (GaAs, with Al_{0.3}GaAs barrier layer) samples grown by using metal organic vapor phase epitaxy after removing the native oxide. Then, deposition of the 2D-array etching masks was conducted. An oxygen treatment was carried out to remove the protein shell, followed by a hydrogen radical treatment to remove the remnant oxide layer. Etching was performed using the NB technique. Defect-free nano-pillars [3] were obtained using both etching masks. It appeared that the nano-pillars with Co masks had a better etching profile than those with Fe masks. Indeed, the nano-pillars formed using Co NPs as the etching masks presented a vertical sidewall whereas the ones formed by using Fe NPs presented an etching profile with tapered angles of about 82°. Moreover, we have successfully achieved 15-nm-in-diameter and over 100-nm-high pillars by NBE process. The average height of the nano-pillars was larger when the Co masks were used. These results suggest that the etching selectivity of Co NPs is higher than that of Fe NPs. The maximum density of the nano-pillars was up to 5x10¹⁰ cm⁻² and did not seem dependent on the chemical nature of the etching mask. The most important parameter for achieving high density, over that of conventional QDs grown by molecular beam epitaxy, is the interaction between the cores and the GaAs surface rather than the etching selectivity. The results showed that III-V compound nanodisk devices can be realized by this defect free top-down nanoprocess.

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4:40pm PS-ThA9 Conductive Carbon Film Formation at Low Temperature (R. T.) using Neutral-Beam-Enhanced Chemical-Vapor-Deposition, Y. Kikuchi, Tohoku University and Tokyo Electron, Japan, S. Samukawa, Tohoku University, Japan

Conductive carbon material such as graphite film is one of the primary materials used as an alternative for metal electrodes in various devices. However, it is difficult to precisely control their properties at low temperature depositions using conventional plasma-enhanced chemical vapor deposition (PECVD). We have developed a neutral-beam-enhanced chemical vapor deposition (NBECVD) process as an alternative to the conventional PECVD process for forming conductive carbon film to solve this problem. NBECVD can almost completely eliminate the irradiation of UV photons and electrons on the substrate surface by using a carbon aperture, resulting in a damage-free deposition process. Moreover, the NBECVD can form a film through the surface polymerization caused by the bombardment of an energy-controlled Ar neutral beam on a surface with absorbed precursors. We previously proposed controlling the molecular-level structures in SiOCH film by using the NBECVD process, which can control the film properties (k-value and modulus). Since the bombardment energy of the neutral beam can be precisely controlled, selective dissociation of the weak chemical bonds in the precursors is possible, which enables us to control the precursor structure when designing the film structure.

In this study, we used toluene as the precursor to grow an aromatic hydrocarbon structure in the film to obtain the conductive properties. As a result, we formed highly conductive carbon films using a low temperature process.

5:00pm PS-ThA10 Numerical Simulation of Total Processes of Neutral Beam Etching from Generation of Neutral Beam by Collision of Ions against Graphite Sidewall to 3-dimensional Etching Profile, N. Watanabe, S. Ohtsuka, Mizuho Information & Research Inst., Japan, S. Mochizuki, Mathematical Systems, Japan, T. Kubota, Tohoku Univ., Japan, T. Iwasaki, Y. Iriye, K. Ono, Mizuho Information & Research Inst., Japan, S. Samukawa, Tohoku Univ., Japan

Neutral beam is an indispensable technology for fabrication of future nano-devices. Especially, a neutral beam source developed by Prof. Samukawa can achieve high neutralization efficiency, controllable energy, and realistic flux. It can perform damage-free processes and is expected to be used in mass production. To achieve production of such future devices, etching simulation is indispensable.

To construct the etching simulation by the neutral beam, simulations of (1) neutral beam generation process by collision of ions from plasma against graphite aperture wall, (2) energy and angular distributions and trajectories of ions and neutral beams passing through the aperture, (3) surface reactions such as etching and deposition, and (4) 3-dimensional etching profile

evolution are needed. We performed these simulations and combined into an etching simulation.

First principles calculation was performed to simulate the neutralization process of chlorine ions. By using a larger unit cell, a planar electronic state which is located about 0.4 nm apart from the graphene sheet was found. Also, it was found that electrons emitted from chlorine particles were absorbed by the planar electronic state. It seems that the state plays an important role in a neutralization process. We have calculated neutralization efficiencies as a function of incident energy, incident angle, and number of collisions.

Based on the result, energy and angular distributions of neutral beam were calculated. In the stage of surface reaction simulation, reactions such as radical adsorption, desorption of products, beam-assisted reaction, physical sputtering, carbon adsorption, and so on were considered. Finally 3-dimensional etching simulator was developed by these results. By using the simulator we could reproduce the experimental results such as aperture aspect ratio dependence and bias dependence.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

5:20pm **PS-ThA11 Controlling the Attributes of Electron Beam Generated Processing Plasmas**, *D.R. Boris, E.H. Lock, R.F. Fernsler, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas have a variety of unique features that make them distinctive plasma sources for materials processing. They are characterized by high plasma density, very low electron temperature, and unique gas phase chemistries that distinguish them from discharge based plasmas. This work presents measurements from suite of diagnostics (RF impedance probes and Langmuir probes, optical emission spectroscopy (OES), and energy resolving mass spectrometer) used to characterize the unique features of electron beam generated plasmas. The focus will be on the important role that gas chemistry plays in determining plasma parameters (kT_e , V_p , ion energy distribution) and the resulting flexibility of the processing system.

5:40pm **PS-ThA12 Time-resolved Discharge Observation of an Argon Plasma Generated by Commercial Electronic Ballast for Remote Plasma Removal Process**, *T. Cho, Y. Sen, R. Bokka, S. Park, D. Lubomirsky, S. Venkataraman*, Applied Materials Inc.

Recently, a remote plasma reactor has been widely used to clean the wafer surface and especially for the removal of the silicon dioxide or silicon nitride over silicon with high selectivity in semiconductor manufacturing industry. In a remote plasma process, plasma is generated within a plasma reactor and delivers only radicals to the process chamber. Absence of plasma in the process region decreases the physical damages of the substrate by ion bombardment and the radicals created by the plasma results in chemical reactions at wafer surface. For a stable supply of radicals to process chamber, a plasma reactor has to be designed very carefully. In Applied Materials, Inc, the plasma reactor adopting a hollow cathode type electrode is being used as a remote plasma source. An argon plasma generated between the cone-shaped electrode powered by commercial electronic ballast and grounded plane electrode has been investigated. Since the electronic ballast has positive and negative cycle in a period, two different discharge modes of remote plasma reactor - the normal glow discharge mode and the hollow cathode discharge mode - have been observed. The hollow cathode discharge mode has wider operation window in gas pressure than the glow discharge one. The glow discharge started to be extinguished at higher pressure than 4.1 Torr and turned suddenly to another hollow cathode discharge mode in the holes on ground plate, while the hollow cathode discharge mode kept growing until 10 Torr. These results show that the stable operation window of the system could be defined by the glow discharge mode rather than the hollow cathode discharge mode and could be improved by optimizing the applied voltage waveform and electrode configuration.

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Bezares, F.: GR+AS+BI+PS+SS-ThA6, 52
Bhargava, N.: EM+AS+PS+TF-ThM2, 41
Bieber, T.: PS-TuP29, 30
Bielefeld, J.D.: EM+AS+PS+TF-ThM9, 42
Bierber, T.: SE+PS-ThM9, 48
Biolsi, P.: PS1-TuM5, 17; PS2-TuA8, 26; PS2-TuM12, 20; PS-MoA1, 11; PS-MoM11, 8
Blackwell, J.M.: EM+AS+PS+TF-ThM5, 42
Blanc, R.: PS1-TuA7, 24; SE+PS-ThM6, **48**
Blechle, J.M.: PS-WeM4, **34**
Bo, T.C.: PS-MoA11, 13
Bobadilla, A.: GR+AS+BI+PS+SS-ThA3, 51
Boffard, J.B.: PS1-TuA11, 24; PS-TuP14, 28
Bokka, R.: PS-ThA12, 55
Bondaz, A.: EM+AS+PS+TF-ThM6, 42
Bongers, W.: EN+AS+PS-TuA11, 21
Bongiorno, A.: GR+AS+BI+PS+SS-ThA10, 52

Booth, J.-P.: PS+TF-MoA1, 9; PS1-TuA2, **23**
Boris, D.R.: PS-ThA11, **55**
Bossert, J.: SE+PS-WeA7, 37
Boufnichel, M.: PS2-TuA3, 25; PS-TuP1, 27
Boutaud, B.: PS2-TuA4, 25
Bower, S.: MS+AS+BA+BI+PS+TF-TuM11, 16
Braithwaite, N.St.J.: PS1-TuA7, 24; PS-WeA9, **36**
Bratescu, M.A.: PS+AS+NS+SS-ThM6, **44**
Bray, J.: PS-TuP23, 29
Brehmer, F.: EN+AS+PS-TuA11, 21; PS1-TuA12, 24
Breit, S.: PS-MoA7, 12
Brennen, R.: MS+AS+BA+BI+PS+TF-TuM1, 15
Brichon, P.D.: PS-ThM2, **45**
Brigg, W.J.: PS-TuP21, 29
Brihoum, M.: PS1-TuA7, 24; PS2-TuM3, 19
Brink, M.: MS+AS+BA+BI+PS+TF-TuM3, 16;
PS-MoA6, 12
Brizzi, S.: EM+PS-TuM10, 15
Brodsky, M.J.: PS2-TuM11, 20
Brown, C.: TF+PS-ThM6, 49
Bruce, R.L.: MS+AS+BA+BI+PS+TF-TuM3, 16;
PS-MoA8, **12**; PS-MoM2, 6; PS-WeM1, 33
Bruneau, B.: PS+TF-MoA1, 9
Bultman, J.E.: SE+PS-ThM5, 47
Burns, S.: PS2-TuM11, 20
Bussmann, K.: GR+EM+NS+PS+SS+TF-MoM3, 2
Butler, J.: MS+AS+BA+BI+PS+TF-TuM11, 16

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Cabral, C.: PS-MoA6, 12
Caldwell, J.: GR+AS+BI+PS+SS-ThA6, 52
Campbell, S.A.: EN+PS+TF-MoM4, 1
Cantone, J.: PS2-TuM9, 20
Cao, J.: PS-TuP11, 27
Carr, L.: MS+AS+BA+BI+PS+TF-TuM1, **15**
Caubet, P.: EM+PS-TuM2, 14; PS+TF-MoA8, 10
Chabal, Y.J.: GR+AS+BI+PS+SS-ThA10, 52
Chabert, P.: PS1-TuA2, 23
Chaker, M.: PS-MoM8, 7
Chakrapani, V.: PS2-TuA8, 26
Chan, B.T.: MS+AS+EM+NS+PS+TF-MoA6, 9
Chandhok, M.: EM+AS+PS+TF-ThM9, 42
Chang, C.M.: PS-TuP26, 30
Chang, J.P.: PS2-TuA7, 26; PS-MoM10, 7
Chaukulkar, R.P.: PS+AS+NS+SS-ThM3, **43**
Chen, H.Y.: PS+AS+BI+SE-MoM4, 4
Chen, J.: EL+AS+EN+PS+SS+TF-ThM4, 40
Chen, J.H.: PS-MoA3, 12
Chen, J.Z.: SE+PS-WeA12, **38**
Chen, K.: PS2-TuA7, **26**; PS-MoM10, 7
Chen, L.: PS1-TuM1, **16**; PS-TuP19, 29; PS-TuP20, 29
Chen, P.L.: PS-TuP26, 30
Chen, Y.Y.: EM+PS-TuM5, 14
Chen, Z.Y.: PS1-TuM1, 16
Cheng, C.: PS+TF-MoA3, 10
Cheng, I.C.: SE+PS-WeA12, 38
Cheng, Y.L.: PS-MoA11, **13**
Chernomordik, B.D.: EN+PS+TF-MoM9, 2
Cheung, D.: PS-MoM6, 7
Chew, S.A.: EM+PS-TuM10, 15
Chiba, Y.: PS2-TuA8, 26; PS-MoA1, 11
Chiou, P.W.: PS-TuP8, 27
Chirita, V.: TF+PS-ThM11, 50
Cho, T.: PS-ThA12, **55**
Cho, T.S.: SE+PS-WeA9, 38
Choe, H.: PS-TuP22, **29**
Chou, C.C.: PS-TuP8, 27
Chung, T.-Y.: PS+AS+BI+SE-MoM11, 6
Ciobanu, C.V.: GR+AS+BI+PS+SS-ThA1, 51
Clarke, J.S.: EM+AS+PS+TF-ThM5, 42;
EM+AS+PS+TF-ThM9, 42
Cleveland, E.: PS-ThA7, **54**
Clima, S.: EM+PS-TuM5, **14**
Cohen, P.I.: GR+EM+NS+PS+SS+TF-MoM1, 2

Colburn, M.E.: MS+AS+EL+EM+PS+TF-TuA4, 22
Cole, C.: MS+AS+EL+EM+PS+TF-TuA9, 22
Cole, J.: PS-TuP18, **28**
Collins, K.: PS-ThM5, 46
Collins, R.W.: EL+AS+EN+PS+SS+TF-ThM4, 40
Colombo, L.: MS+AS+EM+NS+PS+TF-MoA1, **9**
Conley, Jr., J.F.: EM+PS-WeM10, 33
Conrad, E.H.: GR+EM+NS+PS+SS+TF-MoM1, 2
Cotte, J.: MS+AS+BA+BI+PS+TF-TuM3, 16
Creatore, M.: SE+PS-WeA8, 38
Creyghton, Y.L.M.: SE+PS-WeA10, 38
Cruz, J.: PS-TuP34, 31
Cuddy, M.F.: PS-WeM4, 34
Cullen, P.J.: SE+PS-WeA4, 37
Culver, C.L.: PS1-TuA11, 24
Cunge, G.: PS1-TuA7, **24**; PS-ThM2, 45; PS-WeM6, 34; SE+PS-ThM6, 48
Curreli, D.: PS-TuP12, 27; TF+PS-ThM10, 50
Currie, M.: GR+EM+NS+PS+SS+TF-MoM3, 2

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Daniels, S.: PS1-TuA1, 23
Darnon, M.: PS1-TuA7, 24; PS-ThM2, 45; SE+PS-ThM6, 48
Davis, R.C.: TF+PS-ThM2, 49; TF+PS-ThM6, 49;
TF+PS-ThM9, 49
Davydova, A.: PS1-TuA7, 24; PS-WeM6, **34**
De Keyser, P.: PS-TuP29, 30
De Keyser, P.: SE+PS-ThM9, 48
De Marnette, J.-F.: PS-MoA9, 12
de Peuter, K.: PS+AS+NS+SS-ThM3, 43
Degraeve, R.: EM+PS-TuM5, 14
Delattre, P.A.: PS+TF-MoA1, 9
Delcorte, A.: PS+AS+BI+SE-MoM5, 5
Delfour, L.: PS-WeM6, 34
DeLong, E.: EL+AS+EN+PS+SS+TF-ThM12, 41
Demidov, V.: PS-WeM5, 34
Deng, D.D.: EN+PS+TF-MoM9, 2
Deschamps, F.: PS+AS+NS+SS-ThM9, 44
Despiau-Pujo, E.: PS1-TuA7, 24; PS-ThM2, 45;
PS-WeM6, 34
Devant, L.: PS+AS+NS+SS-ThM9, 44
Devashayam, A.: PS-TuP12, 27
DiMeglio, J.: EN+AS+PS-TuA3, 21
Dittman, R.: EM+PS-WeM1, 32
Donegan, M.: SE+PS-WeA4, 37
Donnelly, V.M.: PS1-TuA9, 24; PS1-TuM3, 17;
PS1-TuM4, 17
Doris, B.: PS2-TuM9, 20
Dowling, D.P.: SE+PS-WeA4, 37
Droopad, R.: EM+PS-TuM3, **14**; EM+PS-TuM9, 15
Dubois, G.: EM+AS+PS+TF-ThM3, **42**
Dufour, T.: PS+AS+BI+SE-MoM5, 5;
PS+AS+NS+SS-ThM9, 44
Dupuy, E.: PS2-TuM3, 19
Dussart, R.: PS2-TuA1, **25**; PS2-TuA4, 25; PS-TuP1, 27
Dutta, D.: EM+AS+PS+TF-ThM2, 41
Dylla, H.F.: PS-WeA1, **36**
Dzarasova, A.: PS-TuP21, **29**

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Economou, D.J.: PS1-TuA9, **24**; PS1-TuM3, 17;
PS1-TuM4, 17
Eddy, C.: GR+EM+NS+PS+SS+TF-MoM3, 2
Edmonds, M.: EM+PS-TuM9, **15**
Edström, D.: TF+PS-ThM11, 50
Engelmann, S.U.: PS-MoA8, 12; PS-MoM2, 6; PS-WeM1, 33
Engeln, R.: EN+AS+PS-TuA11, 21; PS1-TuA12, 24
Engtrakul, C.: TF+PS-ThM5, 49
Eriguchi, K.: PS-MoM1, 6; PS-ThM1, 45
Estrada-Raygoza, I.C.: MS+AS+EL+EM+PS+TF-TuA4, **22**; PS2-TuM9, 20

Eun, C.: PS+AS+BI+SE-MoM3, 4

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Faken, D.: PS-MoA7, 12
Fantini, A.: EM+PS-TuM5, 14
Farah, S.: MS+AS+BA+BI+PS+TF-TuM11, 16
Farber, D.: PS-WeM3, 34
Farrar, P.: MS+AS+EM+NS+PS+TF-MoA10, 9
Fazio, W.: TF+PS-ThM2, 49
Feldman, L.C.: GR+EM+NS+PS+SS+TF-MoM1, 2
Feng, P. X.-L.: PS+AS+NS+SS-ThM12, 45
Fernandez, M.C.: PS2-TuA3, 25
Fernsler, R.F.: PS-ThA11, 55
Feurprier, Y.P.: PS-MoA1, 11
Fisher, B.: GR+EM+NS+PS+SS+TF-MoM6, 3
Fisher, E.R.: PS+AS+BI+SE-MoM10, 5; PS-WeM4, 34; TF+PS-ThM1, 49
Flatt, J.: MS+AS+BA+BI+PS+TF-TuM11, 16
Foucher, M.: PS1-TuA2, 23
Fouchier, M.: PS2-TuM3, 19
Fox-Lyon, N.A.: PS-WeM3, 34; PS-WeM5, 34
Franek, J.: PS-WeM5, 34
Fridde, P.: PS2-TuM9, 20; PS-MoA3, 12
Fried, D.: PS-MoA7, 12
Fried, M.: EL+AS+EN+PS+SS+TF-ThM5, 40
Fritz, G.: PS-MoA6, 12
Fujiwara, H.: EL+AS+EN+PS+SS+TF-ThM1, 40
Fukasawa, M.: PS-MoM1, 6; PS-TuP30, 31
Fukiage, N.: TF+PS-ThM12, 50
Fukidome, H.: GR+EM+NS+PS+SS+TF-MoM4, 3
Fuller, N.: PS-MoA8, 12
Funk, M.: PS1-TuM1, 16

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Gaddam, S.: PS-WeM11, 35
Gahan, D.: PS1-TuA3, 23; PS1-TuA7, 24
Gaman, C.: PS1-TuA1, 23
Gangwar, R.K.: SE+PS-ThM11, 48
Gaskill, D.K.: GR+EM+NS+PS+SS+TF-MoM3, 2
Gassilloud, R.: PS+TF-MoA8, 10
Gherardi, N.: PS+AS+NS+SS-ThM10, 44; SE+PS-ThM11, 48
Ghibaud, G.: EM+PS-TuM2, 14
Ghosh, S.: PS+AS+NS+SS-ThM12, 45
Gianchandani, Y.: PS+AS+BI+SE-MoM3, 4
Gibson, D.: MS+AS+BA+BI+PS+TF-TuM11, 16
Gidley, D.: EM+AS+PS+TF-ThM2, 41
Gignac, M.S.: MS+AS+BA+BI+PS+TF-TuM3, 16
Go, D.B.: PS+AS+BI+SE-MoM1, 4; PS+AS+BI+SE-MoM6, 5
Goeckner, M.J.: PS-TuP27, 30
Goede, A.P.H.: EN+AS+PS-TuA11, 21
Goldblatt, M.S.: MS+AS+BA+BI+PS+TF-TuM3, 16
Gözlhäuser, A.: GR+EM+NS+PS+SS+TF-MoM8, 4
Goss, M.: PS2-TuM9, 20
Gosset, N.: PS-TuP1, 27
Gottscho, R.A.: PS-WeA11, 36
Gouma, P.: MS+AS+EL+EM+PS+TF-TuA10, 22
Goux, L.: EM+PS-TuM5, 14
Govoreanu, B.: EM+PS-TuM5, 14
Graham, W.S.: PS-MoM2, 6
Granzer, T.: SE+PS-ThM12, 48
Graswinkel, M.: EN+AS+PS-TuA11, 21
Graves, D.B.: PS+AS+BI+SE-MoM11, 6; PS-WeM6, 34
Greene, J.E.: TF+PS-ThM11, 50
Greiner, K.: PS-MoA7, 12
Griffin, T.: PS-TuP23, 29
Gronheid, R.: MS+AS+EM+NS+PS+TF-MoA6, 9; PS-MoA9, 12
Gudmundsson, J.T.: PS+TF-MoA9, 11
Guillorn, M.: MS+AS+BA+BI+PS+TF-TuM3, 16
Guisinger, N.P.: GR+EM+NS+PS+SS+TF-MoM6, 3
Gunawan, A.A.: EN+PS+TF-MoM4, 1; EN+PS+TF-MoM9, 2
Gundersen, M.: EN+AS+PS-TuA9, 21
Gupta, M.: TF+PS-ThM3, 49

Gupta, R.: PS-MoM3, 6

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Haack, L.P.: SE+PS-WeA3, 37
Haass, M.: PS1-TuA7, 24
Haensch, W.: MS+AS+EM+NS+PS+TF-MoA3, 9
Haga, H.: PS2-TuA8, 26
Haga, T.: PS-TuP24, 29
Hamaguchi, S.: PS+TF-MoA10, 11; PS2-TuM5, 19; PS-ThA3, 53; PS-TuP30, 31; PS-WeM9, 35
Hannon, J.: GR+EM+NS+PS+SS+TF-MoM3, 2; MS+AS+BA+BI+PS+TF-TuM11, 16
Hansen, R.S.: TF+PS-ThM6, 49
Haran, B.: MS+AS+EL+EM+PS+TF-TuA9, 22
Hart, C.: PS+AS+BI+SE-MoM11, 6
Hawker, M.: PS+AS+BI+SE-MoM10, 5
Hayashi, H.: PS2-TuA11, 26; PS-MoM4, 7
Hayes, A.V.: PS-TuP12, 27
Hazeghi, A.: PS1-TuM6, 17
He, H.: PS2-TuM9, 20
Heissl, M.: SE+PS-ThM12, 48
Henderson, C.: MS+AS+EL+EM+PS+TF-TuA3, 22
Hernández, S.: GR+AS+BI+PS+SS-ThA6, 52
Hersam, M.C.: GR+EM+NS+PS+SS+TF-MoM6, 3
Heske, C.: EN+PS+TF-MoM1, 1
Heyne, M.H.: PS-MoA9, 12
Higo, A.: PS-ThA8, 54
Hiramoto, M.: PS-TuP33, 31
Hofmann, T.: EL+AS+EN+PS+SS+TF-ThM9, 40
Hogan, C.J.: PS+AS+NS+SS-ThM5, 44
Hohle, C.: PS2-TuM1, 18
Hoinkis, M.: PS-MoA6, 12
Holoan, A.M.: PS1-TuA1, 23
Honda, M.: PS2-TuM2, 19
Hong, J.: SE+PS-WeA9, 38
Hopkins, M.B.: PS1-TuA3, 23
Hori, M.: PS1-TuA10, 24; PS2-TuA11, 26; PS-ThA6, 53; PS-TuP11, 27; PS-WeM2, 34
Horiba, K.: GR+EM+NS+PS+SS+TF-MoM4, 3
Horiguchi, N.: EM+PS-TuM10, 15
Hou, T.H.: EM+PS-TuM11, 15
Houssiau, L.: PS+AS+NS+SS-ThM9, 44
Hsiao, C.-N.: PS-TuP26, 30
Hsieh, C.C.: PS-TuP16, 28
Hsieh, C.H.: PS-TuP16, 28
Hsieh, J.H.: PS+TF-MoA2, 10
Hsu, C.C.: PS+AS+BI+SE-MoM4, 4; PS-TuP8, 27; SE+PS-WeA12, 38
Hsu, C.W.: EM+PS-TuM11, 15
Huang, J.F.: PS-MoA11, 13
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Hultman, L.: TF+PS-ThM11, 50

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Ide, T.: GR+EM+NS+PS+SS+TF-MoM4, 3
Igarashi, K.: GR+AS+BI+PS+SS-ThA4, 51
Iijima, T.: GR+AS+BI+PS+SS-ThA8, 52
Imamura, T.: PS-MoM4, 7
Iriye, Y.: PS-ThA10, 54
Ishibashi, K.: PS-ThM9, 46
Ishikawa, K.: PS1-TuA10, 24; PS2-TuA11, 26; PS-ThA6, 53; PS-TuP11, 27; PS-WeM2, 34
Iski, E.: GR+EM+NS+PS+SS+TF-MoM6, 3
Isobe, M.: PS-ThA3, 53; PS-TuP30, 31
Itagaki, N.: PS+TF-MoA11, 11
Ito, K.: MS+AS+EL+EM+PS+TF-TuA9, 22
Ito, M.: PS1-TuA10, 24
Ito, T.: PS2-TuM5, 19; PS-TuP30, 31
Itou, A.: PS-MoA8, 12; PS-MoM2, 6
Iwao, T.: PS-ThM9, 46
Iwasaki, T.: PS-ThA10, 54; PS-ThM12, 47

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Jacob, A.: PS2-TuM9, 20
Jacobs, B.: PS-MoM6, 7
Jahnes, C.: MS+AS+BA+BI+PS+TF-TuM3, 16
Jandhyala, S.: GR+AS+BI+PS+SS-ThA7, 52
Jang, L.: MS+AS+EL+EM+PS+TF-TuA9, 22
Jariwala, B.N.: GR+AS+BI+PS+SS-ThA1, 51
Jensen, B.D.: TF+PS-ThM2, 49; TF+PS-ThM9, 49

Jeon, J.H.: PS-TuP22, 29

Jernigan, G.G.: GR+EM+NS+PS+SS+TF-MoM3, 2
Jezewski, C.J.: EM+AS+PS+TF-ThM9, 42
Job, N.: PS+AS+NS+SS-ThM9, 44
Johnson, E.V.: PS+TF-MoA1, 9
Johnson, M.: EN+PS+TF-MoM10, 2
Joseph, E.A.: MS+AS+BA+BI+PS+TF-TuM3, 16; PS-MoA6, 12; PS-MoA8, 12; PS-MoM2, 6; PS-WeM1, 33
Joubert, O.: PS1-TuA7, 24; PS-ThM2, 45; SE+PS-ThM6, 48
Juhel, M.: EM+PS-TuM2, 14
Jung, J.: EM+PS-WeM4, 32
Jung, R.: MS+AS+EL+EM+PS+TF-TuA9, 22
Junkermeier, C.: GR+AS+BI+PS+SS-ThA6, 52
Jurczak, M.: EM+PS-TuM5, 14
Jurczyk, B.: TF+PS-ThM10, 50
Jussot, J.: PS2-TuM3, 19

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Kaganovich, I.D.: PS-TuP19, 29; PS-TuP20, 29
Kaiser, U.: GR+EM+NS+PS+SS+TF-MoM8, 4
Kakaroglou, A.: SE+PS-WeA7, 37
Kamataki, K.: PS+TF-MoA11, 11
Kaminski, M.: GR+AS+BI+PS+SS-ThA3, 51
Kamon, M.: PS-MoA7, 12
Kanakasabapathy, S.: MS+AS+EL+EM+PS+TF-TuA9, 22; PS2-TuA8, 26; PS2-TuM11, 20
Kanan, M.: EN+AS+PS-TuA1, 21
Kanarik, K.J.: PS-WeA11, 36
Kang, H.: MS+AS+EL+EM+PS+TF-TuA9, 22
Kang, S.: PS+AS+NS+SS-ThM5, 44
Kang, S.Y.: TF+PS-ThM12, 50
Kao, C.-L.: PS-MoM5, 7
Kao, P.K.: PS-TuP8, 27
Karahashi, K.: PS+TF-MoA10, 11; PS2-TuM5, 19; PS-TuP30, 31; PS-WeM9, 35
Karakas, E.: PS1-TuA9, 24
Karpowicz, T.: EM+AS+PS+TF-ThM6, 42
Kasi, H.: PS-WeM11, 35
Kathrein, M.: SE+PS-ThM12, 48
Katz, K.: PS1-TuM6, 17
Kawai, Y.: GR+EM+NS+PS+SS+TF-MoM4, 3
Keisuke, S.: PS2-TuM12, 20
Kelber, J.: PS-WeM11, 35
Kelkar, S.S.: PS+AS+NS+SS-ThM11, 44
Kenney, J.: PS-ThM5, 46
Kent, T.: EM+PS-TuM9, 15
Keville, B.J.: PS1-TuA1, 23
Khrabrov, A.: PS-TuP19, 29; PS-TuP20, 29
Kievit, O.: SE+PS-WeA10, 38
Kikuchi, Y.: PS-ThA9, 54
Killeen, K.: MS+AS+BA+BI+PS+TF-TuM1, 15
Kim, H.J.: EM+PS-WeM4, 32
Kim, J.: EM+PS-WeM9, 33; GR+AS+BI+PS+SS-ThA7, 52
Kim, S.: PS-TuP17, 28; PS-TuP23, 29
Kim, S.J.: EM+PS-WeM4, 32
Kim, T.: PS2-TuA7, 26; PS-MoM10, 7
Kim, Y.: GR+EM+NS+PS+SS+TF-MoM5, 3
King, S.W.: PS-MoA10, 13
Kinoshita, T.: GR+EM+NS+PS+SS+TF-MoM4, 3
Kintaka, H.: PS1-TuM5, 17
Király, B.T.: GR+EM+NS+PS+SS+TF-MoM6, 3
Kitajima, T.: GR+AS+BI+PS+SS-ThA2, 51; PS1-TuM12, 18; PS-TuP24, 29
Knoll, A.J.: PS-WeM3, 34; PS-WeM5, 34
Ko, A.: MS+AS+EL+EM+PS+TF-TuA4, 22; MS+AS+EL+EM+PS+TF-TuA9, 22; PS2-TuA8, 26; PS-MoA1, 11
Kobayashi, K.: PS2-TuM2, 19
Koepke, M.: PS-WeM5, 34
Koga, K.: PS+TF-MoA11, 11
Koirala, P.: EL+AS+EN+PS+SS+TF-ThM4, 40
Kolbeck, J.: PS1-TuM11, 18
Kometani, R.: PS-ThA6, 53; PS-TuP11, 27
Kondo, H.: PS1-TuA10, 24; PS2-TuA11, 26; PS-ThA6, 53; PS-TuP11, 27; PS-WeM2, 34
Koster, N.B.: SE+PS-WeA10, 38

- Kotsugi, M.: GR+EM+NS+PS+SS+TF-MoM4, 3
 Kozicki, M.N.: EM+PS-WeM5, 32
 Krishnan, M.: MS+AS+BA+BI+PS+TF-TuM3, 16
 Krishtab, M.: PS-ThA4, 53
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 Kumar, A.: PS+AS+NS+SS-ThM5, 44
 Kumar, K.: MS+AS+EL+EM+PS+TF-TuA9, 22;
 PS1-TuM5, 17; PS2-TuA8, 26; PS2-TuM12,
 20; PS-MoA1, 11; PS-MoM11, 8
 Kummel, A.C.: EM+PS-TuM1, 14; EM+PS-
 TuM9, 15
 Kuo, P.J.: PS-TuP8, 27
 Kuo, Y.: EM+PS-WeM11, 33
 Kurasch, S.: GR+EM+NS+PS+SS+TF-MoM8, 4
 Kushner, M.J.: PS+AS+BI+SE-MoM3, 4; PS1-
 TuM2, 16; PS1-TuM4, 17; PS-ThM3, 46; PS-
 WeA7, 36
 Kusuda, Y.: PS-TuP33, 31
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- Laderman, S.: MS+AS+BA+BI+PS+TF-TuM5, 16
 Ladroue, J.: PS-TuP1, 27
 Lafleur, T.: PS+TF-MoA1, 9
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 Larriba-Andaluz, C.: PS+AS+NS+SS-ThM5, 44
 Lawson, R.: MS+AS+EL+EM+PS+TF-TuA3, 22
 Lazzarino, F.: PS-ThA4, 53
 Lazzaroni, R.: PS+AS+BI+SE-MoM5, 5
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