Electronic Materials and Photonics
Room 102A - Session EM+NS+PS+SS+TF-MoM

Growth and Devices Technology of Group III-Nitrides

Moderators: Nikolaus Dietz, Georgia State University, Shalini Gupta, Northrop Grumman ES

8:20am **EM+NS+PS+SS+TF-MoM1 Development of AlGaN based UV Laser Diodes**, ***Ronny Kirste***, Adroit Materials; *B. Sakar, A. Franke,* NCSU; *J. Tweedie,* Adroit Materials; *Z. Bryan, I. Bryan,* NCSU; *S. Mita,* Adroit Materials; *R. Collazo, Z. Sitar,* NCSU **INVITED**

UV laser diodes are widely desired for many important applications such as chemical and biological sensing, non-line of sight communications, and DNA tagging. Design and fabrication of AlGaN based laser diodes is the most promising pathway for next generation UV lasers but challenges for these devices are many including low n- and p-conductivity, absorbing injection layers, and non-ohmic contacts. Here, we present recent advances in the growth and fabrications of UV laser diodes. The presentation will cover the most important steps that are necessary to achieve electrically injected UV laser diodes. These include: AlGaN epitaxy, doping, fabrication, and design.

As an advancement over most existing approaches, we pursue the growth of our device structures on single crystalline AlN substrates which allows for low dislocation densities < 10^4 cm^2. Any such device fabrication is started with the growth of an AlN homoepitaxial layer. It is demonstrated that this epitaxial layer can be grown with a dislocation density that follows that of the substrate and no interface between layer and substrate is observed in TEM, which indicates true homoepitaxy. Subsequent growth of AlGaN layers with Al content ranging 50-85% is shown to be pseudomorphic. An excellent control of the AlGaN surface morphology is demonstrated using a supersaturation scheme and bilayer steps as needed for highly efficient MQWs are achieved. MQWs for emission at wavelengths ranging 240-280 nm are discussed and optically pumped lasing in this region is demonstrated. The chosen approach to grow on AlN is validated by realizing MQWs with an IQE exceeding 90%. In order to achieve electrically injected UV lasing, Al-rich AlGaN is doped and free electron concentrations for the n-cladding with 80% Al-content is shown to be around $8x10^{18}$ cm^{-3}. In contrast, p-doping of AlGaN is much more challenging because of the high activation energy of the Mg acceptor. Consequently, achievable free hole concentration and conductivity of the p-cladding are low. We discuss how these epitaxial layers can be used for realizing laser diodes. Experimental work is supported by simulations and used to direct the UV laser design. Finally, we present electrical data and electroluminescence spectra from fully fabricated diodes and discuss the future challenges that need to be addressed to demonstrate the first electrically injected UV laser diode.

9:00am **EM+NS+PS+SS+TF-MoM3 Low-Temperature PA-ALD Growth Technology for Group III-Nitride Nano-heterostructures and their (Opto)Electronic Device Applications**, ***Necmi Biyikli***, *A. Haider, S. Kizir, P. Deminskyi, M. Yilmaz, S. Bolat, A. Celebioglu, A.K. Okyay, T. Uyar,* Bilkent University, Turkey; *F. Buyukserin, S. Altuntas,* TOBB University of Economics and Technology, Turkey; *I. Yilmaz, K. Khaled,* Turgut Ozal University, Turkey **INVITED**

Being initially developed for an entire different area of use, atomic layer deposition (ALD) became a widespread tool to grow functional films and conformal ultra-thin coatings for numerous applications. Based on self-limiting surface reactions, ALD enabled the low-temperature growth of various materials including dielectrics, semiconductors, and metals. Featuring the capability to deposit wafer-scale uniform semiconductor films at relatively low-temperatures with sub-monolayer thickness control and ultimate conformality makes ALD attractive for the semiconductor community. Towards this end, precursors and growth recipes are developed to deposit crystalline thin films for compound and elemental semiconductors. Conventional thermal ALD techniques as well as plasma-assisted and radical-enhanced ALD techniques have been exploited to achieve decent film quality compatible with device applications.

In this presentation, we give an overview of our research efforts on plasma-assisted ALD-based nanoscale semiconductor research focusing on III-nitrides. We have combined our low-temperature thin-film growth recipes with various nanoscale templates and exploited the conformality feature of ALD technique to fabricate nitride nanostructures. Electrospun polymeric nanofibers have been used to produce flexible polymer/III-nitride core-shell structures which might be used for flexible optoelectronics. In addition, hollow-core multi-shell III-nitride nano-heterostructures are demonstrated as well. Anodized alumina (AAO) templates were utilized to fabricate large-area ordered III-nitride nanostructures including radial heterostructures. Extensive growth and fabrication recipe development and materials characterization details will be presented.

The synthesized III-nitride nanoscale semiconductor materials might find applications in a vast amount of applications including physical and chemical sensing, piezo-electric energy harvesting, photocatalysis, nanoscale and flexible (opto)electronics. As proof-of-principle device demonstrations, we have shown nanofibrous GaN/InN-based photocatalysis, GaN/InN-based chemical (gas) sensing, and nanoscale GaN-based UV photodetectors.

9:40am **EM+NS+PS+SS+TF-MoM5 Structural Qualities of GaN Grown on AlN Buffer Layer by MEPA-MOCVD**, ***Daniel Seidlitz***, *I. Senevirathna, A. Fali, Y. Abate, N. Dietz,* Georgia State University; *A. Hoffmann,* Technical University Berlin, Germany

This study focusses on the influence of Aluminum nitride (AlN) buffer layers on the structural and optoelectronic properties of subsequent overgrown Gallium nitride (GaN) layers, using Migration Enhanced Plasma-Assisted Metal Organic Chemical Vapor Deposition (MEPA-MOCVD).

One challenge in group-III nitride growth is the lattice mismatch between the substrate (e.g. sapphire (Al_2O_3), silicon or silicon carbide) and the group III-Nitride layer as for example GaN. Lattice mismatch imposes compressive strain/stress and influences the crystal quality of subsequent grown group-III nitrides. Inserting an AlN interlayer between the sapphire substrate and the GaN epilayer, transitions the oxygen surface chemistry to a nitrogen surface chemistry, separating surface chemistry related defects from lattice mismatch induced defects, which leads to an improved crystalline quality of the overgrowning GaN layer.

All group III-Nitride layers are grown on sapphire substrates using MEPA-MOCVD. The system design allows the growth of GaN at lower temperatures by using plasma activated nitrogen species (N*/NH*/NHx*) as nitrogen precursor, which are generated by a radio-frequency hollow cathode plasma source (MEAglow™) scalable from 20W up to 600W. The tunable nitrogen plasma source enables to control the kinetic energies of the active nitrogen species in the afterglow region to be directed at the growth surface, where they interact with metalorganic (MO) precursors. The growth process parameter set includes: reactor pressure, growth temperature, pulsed injection of MO- and nitrogen plasma fluxes, plasma species and their energies.

The structural properties of the AlN buffer layers (e.g. local ordering, grain size, surface topography) are analyzed by Atomic Force Microscopy (AFM) and Raman spectroscopy. The film thickness and optoelectronic properties of the AlN and GaN layers are studied Fourier Transform infrared (FTIR) and reflectance spectroscopy. Results are presented on the structural and optoelectronic properties of the GaN layers as function of the process parameters and the properties of the underlying AlN buffer layer.

10:00am **EM+NS+PS+SS+TF-MoM6 Optical and Electrical Characteristics of Gamma-ray Irradiated AlGaN/GaN Heterostructures**, ***MinPrasad Khanal***, *B. Ozden, K. Kim, S. Uprety, V. Mirkhani, L. Shen, K. Yapabandara, A.C. Ahyi, M. Park,* Auburn University

AlGaN/GaN high electron mobility transistors (HEMTs) show their potential immunity toward high energy radiation related damages, making them promising candidates for the radiation hard electronics. The degradation in performance of these devices under radiation exposed environment might be due to different possible effects in the device structure such as strain/stress, generation of dislocation, carrier removal and reduction in two-dimensional-electron-gas (2DEG) concentration.The AlGaN/GaN epi structures grown on 6 inch Si wafer were used and irradiated with 120 MRad doses of gamma-ray produced from ^{60}Co source. The semi-transparent (with 10-15 nm thickness) Ni Schottky diodes and circular HEMT devices were fabricated using un-irradiated and gamma-ray irradiated AlGaN/GaN epi structures. In the case of HEMT devices, Ti/Al/Ni (30/180/40 nm thickness) for the ohmic contact and Ir (15 nm thickness) for the gate contact formation were deposited using dc magnetron sputtering system. Spectroscopic photo current-voltage (IV) measurements both with sub-band gap and above band-gap illumination, micro-Raman/photoluminescence spectroscopy, and transistor characterizations were performed. The spectroscopic photo IV measurements were carried out by applying the variable wavelength ultra-violet (UV) and visible light from Xenon lamp source under reverse bias condition. Sub-bandgap illumination (800 nm-400 nm) provided the information about sub-

bandgap energy levels of defects by relating the change in photocurrent level in response to the applied light spectrum. On the other hand, above bandgap illumination (280 nm-400 nm) utilizes the fact that the penetration depth of a light varies as a function of wavelength. The result showed reduction in photocurrent on the gamma-ray irradiated samples in comparison to the un-irradiated samples, revealing the possibility of creation of extra defects, and hence, decreasing the carrier concentration in the 2DEG. Micro-Raman and photoluminescence (PL) spectroscopic analysis on both the samples were also performed and the results show no substantial change in their spectra, supporting the conclusion from previous scientific reports of radiation resistance of the HEMTs on their bulk structure level. Decrease in drain current and transconductance were observed from the transistor IV measurements, indicating a possible reduction in carrier concentration. It can be concluded that the reduction on photocurrent, drain current level and transconductance after the gamma-ray irradiation are due to the possible creation of some extra defects and decrease of carrier concentration on 2DEG channel.

10:40am **EM+NS+PS+SS+TF-MoM8 Seeded Regrowth for Production of AlN and GaN Substrates by HVPE***, **Jacob Leach**, K. Udwary, G. Dodson, K. Gentry, P. Quayle, T. Schneider, H. Splawn, K. Evans,* Kyma Technologies, Inc. **INVITED**

Freestanding GaN and freestanding AlN remain the substrates of choice for the highest performing vertical high voltage switching devices (>1200V) and UV optoelectronics, respectively. However, the cost of these substrates remains high, availability remains low, and the crystalline quality of these substrates varies depending on the growth technique employed. In particular, the electrical quality of GaN substrates and the UV transparency of AlN substrates depend on the specific growth conditions utilized and it remains a challenge to maintain high crystalline quality while simultaneously realizing high electrical quality or UV transparency. We proposed the use of hydride vapor phase epitaxy (HVPE) as a cloning technique to replicate the high crystalline quality of existing solvothermally grown GaN or physical vapor transport (PVT) grown AlN substrates while maintaining high electrical and optical quality. In this talk, we report Kyma's recent results in the use of the HVPE replication technique for realizing both AlN and GaN substrates.

Plasma Science and Technology
Room 104D - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing

Moderator: Lorenzo Mangolini, University of California Riverside

9:00am **PS+SE-MoM3 Fundamental Characterization of a Low Frequency, Ambient Air, Plasma Jet Discharge***, **Vladimir Milosavljevic,*** Dublin Institute of Technology, Ireland*; L. Scally, J. Lalor, P.J. Cullen,* Dublin Institute of Technology

Plasma discharge in open air has charged species, energetic photons, active radicals, and also a low degree of ionization gas. Interaction of such plasma with surfaces has been a subject of intense study for many decades. In particular, an atmospheric jet plasma system used to solve surface preparation problems. The biggest advantages of such a system are: high density plasma in contrast to corona discharge, no electrical current or filamentary streamers in the plasma jet, broad material application capability, simple host automation integration, low environmental impact, and low thermal load allows low melting point polymers to be treated. Despite the widespread usage of plasma jet technology, it remains largely unknown whether atmospheric plasma maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. In this work optical spectroscopy was used as a diagnostic method due to its non-intrusive nature. In additional to this, surface metrology based on a measurement of the water contact angle (WCA) and surface energy was also engaged.

In this study a high pressure (6 bar) atmospheric plasma jet system, which operates with ambient air chemistry, was employed. The plasma jet operated at a frequency of 60 Hz and used a pencil type beam applicator. The low operation frequency makes this system significantly different from a vast majority of other plasma jets. Namely, at low frequencies (<50 kHz) ions and electrons both oscillate and therefore both contributed in interaction with surfaces. At high frequencies (>50 kHz) heavy ions cannot follow switching fields and therefore only electrons oscillate while ions are relatively stationary which has a huge impact on the plasma sheath dynamics.

The polymer used in this work was polyethylene terephthalate (PET) and was widely used in a variety of industries from food packaging to the electrical, electronics, and biomedical industries. PET could be easily thermally damaged at relatively low temperatures and so a delicate balance must be reached where surface activation of the polymer was maximised, while thermal damage was prevented. The level of polymer surface activation was evaluated based on changes to the WCA of PET samples after plasma treatment. A direct correlation was obtained between the polymer WCA changes and the OES measurement. This correlation may indicate that OES peak intensities can be used as an indicator of the treated polymer WCA, without the need for conventional off-line metrology.

This work was a funded by SFI under the PlasmaGrain project.

9:20am **PS+SE-MoM4 CO_2 Splitting by Dielectric Barrier Discharge at Atmospheric Pressure: Understanding the Influence of Electrical Regimes and Electrical Configurations***, **Alp Ozkan,** T. Dufour,* Université Libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Research group PLASMANT, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) are commonly used to generate cold plasmas at atmospheric pressure. In this experimental work, a flowing tubular DBD is used for the CO_2 splitting into O_2 and CO. The influence of the frequency (from 16 to 28 kHz), the power (from 30 to 100 W), the role of the barrier thickness (2.0, 2.4 and 2.8 mm), the kind of dielectric material (alumina, mullite, pyrex, quartz), and the effect of a pulsed AC discharge (so-called burst mode) are investigated on the filamentary behavior of the plasma and on the CO_2 conversion, by means of mass spectrometry measurements correlated with electrical diagnostics. Their influence on the gas and electrode temperature is also evidenced through optical emission spectroscopy and infrared imaging. A new methodology is developed to investigate the microdischarge properties. For this purpose, electrical measurements, based on a numerical method, are carried out to explain the conversion trends and to characterize the microdischarges through their number (N_{md}), their lifetime (L_{md}), their intensity (i_{pl}) and the induced electrical charge (Q_{pl}) for a given analysis time. These extracted data are usually underestimated or poorly described in literature.

It is shown that, when the applied power is modified, the conversion depends mostly on the Q_{pl} and not on the effective plasma voltage ($V_{pl,eff}$). Similarly, a better conversion is observed at low frequencies, where a more diffuse discharge with a higher $V_{pl,eff}$ than at higher frequency is obtained. Moreover, increasing the barrier thickness decreases the capacitance while preserving the electrical charge. As a result, the voltage over the dielectric (V_{diel}) increases and a larger N_{md} is generated, which enhances the CO_2 conversion. Furthermore, changing the dielectric material of the barrier, while keeping the same dimensions, also affects the conversion. The highest CO_2 conversion and energy efficiency are obtained for quartz and alumina. From the electrical characterization, we clearly demonstrate that the most important parameters are the somewhat higher $V_{pl,eff}$ (yielding a higher electric field and electron energy involved in CO_2 dissociation) for quartz, as well as the higher plasma current (thus larger electron density) and the larger N_{md} (mainly for alumina due its higher roughness, but also for quartz due to its higher V_{diel}). Finally, a comparison between DBD ignited in burst mode and pure AC mode is achieved. Decreasing the duty cycle from 100% (pure AC mode) to 40% leads to a rise in the conversion due to a larger N_{md} and a higher voltage.

9:40am **PS+SE-MoM5 Effect of Structural Variations of the Monomer on the Fast Synthesis of Highly Oxygenated Coatings in an Argon DBD***, **Jérémy Mertens,** F. Reniers,* Université Libre de Bruxelles, Belgium

The use of atmospheric plasma DBD for the synthesis of organic coatings has recently become more and more popular. Their unconventional polymerization pathways allow the synthesis of brand new polymers with specific properties which are strongly dependent on the chemical structure of the injected monomer[1,2].

The goal of this research is the development of an intermediate coating presenting a high surface energy with an important deposition rate in order to improve the adhesion of a resin on aluminum by DBD. Because of their initial structure, anhydrides are seen as ideal candidates for the synthesis of such films. We here present how small variations in their chemical structure can affect their behavior in the discharge and the chemical properties of the coatings. Firstly, the influence of the C/O ratio in the injected monomer is investigated by the use of acetic, propionic and butyric anhydride. The addition of double bonds in the initial structure of

the precursor is then studied using isobutyric and methacrylate anhydride. Surface analyses such as infrared spectroscopy (IRRAS), X-Ray Photoelectron spectroscopy (XPS) and stylus profilometry showed that highly oxygenated coatings could be synthesized when the C/O ratio of the injected monomer was decreased. Nevertheless, high deposition rates could only be reached with the addition of double bonds in the structure of the monomer. By combining these observations with oscilloscope and mass spectrometry measurements of the discharge, a fragmentation/recombination polymerization is suggested for the non-conventionally polymerizable monomers. On the contrary, a mainly radical propagation through the double bonds is proposed for the methacrylate anhydride. The amount of carboxylic components on the surface can be tuned by the addition of an Ar-O_2 post-treatment but is limited by the degradation of the films that leads to the formation of oxidized volatile compounds.

This work was financially supported by the Walloon Region (FLYCOAT project n°131847) and by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

[1] J. Hubert & *al.*, *Journal of Materials Research,* **2015**, 30, 21, 3177-3176

[2] A. Batan & *al., Plasma Processes and Polymers,* **2013**, 10, 857-863

10:00am **PS+SE-MoM6 Quantitative Study of Plasma Electrochemical Reduction of Aqueous Metal Salts***, S. Ghosh, A. Aube, R. O'Toole, R. Hawtof,* ***R.Mohan Sankaran,*** Case Western Reserve University

The possibility of combining ionized gases and ionic solutions to initiate electrochemical reactions in solution with a plasma electrode has been explored for over 100 years. Recently, this idea has been the basis of numerous reports of metal nanoparticle formation when aqueous solutions of metal salts are exposed to a plasma. While this approach has been successfully demonstrated by a range of plasma sources and experimental conditions, the chemistry behind the reactions between plasma and solution species is highly complex and remains poorly understood.

Here, we report quantitative studies of the reduction of aqueous metal salts by a plasma electrode to better understand the reaction kinetics and thermodynamics, analogous to conventional electrochemistry. Kinetic studies were performed by measuring the rate and efficiency of the reduction of a metal salt, silver nitrate. Analogous to weight measurements in electrodeposition of metal thin films, we developed a methodology to measure the mass of the final product, silver (Ag) nanoparticles, by separating the agglomerated particle powder. The reduction efficiency was defined as the actual amount of reduced Ag compared to that predicted by Faraday's law based on the plasma current. We find that in ambient air, the faradaic efficiency for silver nitrate reduction is approximately 80%, and, curiously, the efficiency increases to >100% in a closed reactor cell with an Ar ambient. We interpret these results as follows. Assuming that the chemistry in solution is driven by electrons from the plasma which are directed into solution and can solvate, in ambient air, there is a decrease in the electron flux to the solution because of electron attachment processes involving O_2 gas. Removing air with ambient Ar increases the electron flux and, thus, increases the faradaic efficiency. The surprising efficiency of more than 100% most probably results from an autocatalytic effect whereby reduced Ag (Ag^0) also reduces Ag^+, a mechanism that has been previously reported in radiolytic synthesis of Ag nanoparticles. The thermodynamics of the reduction process was probed by studying a series of metals which have different reduction potentials including copper, iron, and zinc. Successful reduction of the corresponding metal salts for these metals suggests that solvated electrons, which are one of the strongest reducing species, are involved. We will also discuss the respective reduction rates and efficiencies of these metals as compared to Ag.

10:40am **PS+SE-MoM8 LDPE Modified by an Ar/H_2O Dielectric Barrier Discharge: Correlation between Texturization, Wettability and Grafting of Oxygen***, Stéphanie Collette,* Université Libre de Bruxelles, Belgium*; P. Viville,* Université de Mons, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

In the literature, some studies focus on the use of H_2O in plasma discharges because of its potential high reactivity. However, is also known to destabilize plasmas. In this study, the reactivity of water at the interface between the plasma and the surface of the low density polyethylene (LDPE) was investigated. LDPE is chosen as polymer because of its high capacity to be functionalized.

In the first part of this project, we study the water reactivity in atmospheric plasma by injecting H_2O vapor in the discharge of a dielectric barrier discharge, supplied with Ar as carrier gas. OES evidenced the production and the consumption of Ar, O, OH, and N_2 species. They can be quantified as a function of the H_2O flow rate and the treatment time in order to have a better understanding of the reactivity. Some chemical reactions occurring within the discharge can be highlighted. To characterize the discharge itself, current measurements are performed and a high speed camera is used to observe the changes of the discharge (number and size of the streamers).

In the second part of this research, LDPE surfaces exposed to water-containing plasma are characterized by XPS. The measurements of the O 1s peak reveal a strong increase of oxygen from 0% to 16%. XPS Depth profiles evidence the diffusion of O in the subsurface. These results have been compared with WCA measurements expressed as a function of time. Between 0 and 30 s, a strong decrease in the WCA is observed (from 100° to 63°) and can be linked to the rise of the O% (from 0% to 13%). After 30 s, the WCA rapidly decreases to 43° which seems inconsistent with the very slow increase of the O% (almost no rise) observed by XPS. In parallel, AFM measurements show a texturization of the treated LDPE, as the surface roughness increases from 27 nm to 75 nm. The effect observed after 30 s of treatment can be explained by the Wenzel equation:

$\cos \Theta_{app} = r \cos \Theta$

Indeed, the "r" factor in the Wenzel corresponds to the roughness ratio defined as the ratio of true area of the solid surface to the apparent area. Cos Θ can be linked to the polar component of the surface energy and therefore to the oxygen concentration at the surface. The roughness and the oxygen content increase simultaneously with time and the combination of these two factors lead to obtain a higher Cos Θ_{app}. Indeed, the texturization and the grafting of oxygen are correlated by the use of the Wenzel equation thereby allow the understanding of the large decrease of WCA.

This work is supported by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

11:00am **PS+SE-MoM9 Particle-free Fabrication of Stretchable, Electrically Conductive Features by Atmospheric-Pressure Plasma Reduction of Metal-Ion-Containing Polymer Films***, Souvik Ghosh*[*]*, P.X.-L. Feng, C.A. Zorman, R.M. Sankaran,* Case Western Reserve University

Stretchable electrically conductive patterns are an importance class of materials for emerging electronic applications. A relatively well-established approach for their fabrication is printing metal nanoparticle inks on elastomeric polymers to combine the high electrical conductivity of metals with the large mechanical deformability of polymers. However, nanoparticle-based inks have organic-based solvents and contain organic capping molecules to stabilize the nanoparticles, limiting the conductivity of as-printed features and requiring high temperature sintering (>200 °C) to remove the organics, which is not compatible with most polymers. Moreover, the printed metal nanoparticle film may not be well-integrated with the polymer, compromising conductivity at large deformation.

Here, we report a plasma-based approach to producing electrically-conductive metallic features at the surface of polymer films that eliminates the need for nanoparticle inks and has the potential to better integrate metals and polymer. In general, metal salts are initially mixed with a polymer and cast as a thin film. The films are then exposed to a plasma which results in reduction of the metal ions to metal nanoparticles. By using an atmospheric-pressure microplasma jet and rastering the metal-ion-containing polymer film, the reduction is localized and two-dimensional patterns of metal nanoparticles are fabricated.

We initially focused our study on films prepared from silver nitrate ($AgNO_3$) and polyacrylic acid (PAA) which is known to cross-link with metal cations. After exposure to the microplasma, films were characterized by X-ray diffraction (XRD) which confirmed crystallinity from the presence of peaks corresponding to face-centered cubic silver (Ag). Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) revealed that microplasma reduction leads to nanoparticle formation only at the surface of the film. The bulk resistivity of the patterned features was determined by two-point probe measurements and reached values as small as ~1 mΩ-cm.

To obtain stretchable films, two approaches were explored. First, PAA-Ag thin films were cast on top of polydimethylsiloxane (PDMS) - an elastomer, and reduced by the microplasma. Second, we extended our process to a

[*] **Coburn & Winters Student Award Finalist**

rubber polymer (styrene-isoprene-styrene) (SIS) which could be mixed with silver trifluoroacetate to be reduced and form Ag in a single polymer layer. Results for the resistivity as a function of the strain in the various material systems will be presented, as well as a working model for the role of the plasma in the reduction of the metal in the polymer and its final morphology.

11:20am **PS+SE-MoM10 Plasma Polymerised 4-vinyl Pyridine Films with High Charge Density Synthesised in Atmospheric Roll-to-Roll System**, ***Hindrik de Vries,*** FOM institute DIFFER, Netherlands*; W. van Baak, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., Netherlands*; M.C.M. van de Sanden,* FOM institute DIFFER, Netherlands

Nowadays plasma polymerisation is considered as an attractive tool to synthesise ultra-thin organic functional coatings. In this contribution we report for the first time the synthesis of PP thin 4-vinylpyridine containing films synthesised in a roll-to-roll set-up in an atmospheric pressure plasma enhance chemical vapour deposition (AP-PECVD) reactor using low cost nitrogen gas. The general details of the reactor and plasma parameters were described elsewhere [1]. Specific of the present work is the use of a variable short pulse trains. Nitrogen was used as a carrier gas admixed with a variable flow of argon to control the vaporisation rate of 2 monomers: 4-vinylpyridine (4-VP) and divinylbenzene (DVB) to enable copolymerisation reaction. The film properties were tuned by varying the power per injected precursor molecule and the mixing ratio of the 2 monomers. The films were characterized on thickness (spectroscopic ellipsometry), adhesion (tape test), roughness (interferometric microscopy), and wettability (water contact angle). The microstructure of the 4-VP films was assessed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS). The fixed charge was characterised by zeta potential measurements. Film analysis showed that the main feature (pyridine group) was preserved although newly formed peaks in the ATR-FTIR spectrum indicate partial dissociation of the 4-VP. Pulse parameters as well as the DVB [2] flow were studied to improve cross-linking of the film. Zeta potential measurements confirmed the presence of positive charge at the surface. Subsequently, the films were quaternized leading to a further enhancement of the fixed charge on the surface. Recent results will be highlighted and recommendations for further improvement of the atmospheric plasma processing will be discussed.

[1] S.A. Starostin et al. *Plasma Process. and Polym.* 12, no. 6 (2015): 545–54.

[2] R. Yang et al. *Advanced Materials* 26, no. 11 (2014): 1711–18.

11:40am **PS+SE-MoM11 Plasma-Surface Interactions in Atmospheric Pressure Plasmas: *In Situ* Measurements of Local Excitations in Thin Films**, ***Scott Walton,*** Naval Research Laboratory*; B.M. Foley,* University of Virginia*; D.R. Boris, E.D. Gillman, S.C. Hernández,* Naval Research Laboratory*; A. Giri,* University of Virginia*; Tz.B. Petrova, G.M. Petrov,* Naval Research Laboratory*; P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physicochemical changes associated plasma-based materials processing. The unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure the electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the excited electrons propagate radially from the point of contact. These results, in conjunction with plasma characterization, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

Plasma Science and Technology
Room 104B - Session PS-MoM
Advanced FEOL/Gate Etching

Moderator: Ankur Agarwal, Applied Materials, Inc.

8:20am **PS-MoM1 Novel Etch Strategies for Sidewall Image Transfer**, ***Sonam Sherpa,*** *P. Chan, A. Ranjan,* Tokyo Electron Ltd.

Sidewall image transfer (SIT) is an indirect patterning method that involves the deposition and etching of silicon nitride spacer to achieve sub-lithographic linewidths. Current approaches to etch silicon nitride spacer face two main challenges --— footing and corner rounding. Solution to these problems requires a non-polymerizing chemistry that must be anisotropic and yet avoids the adverse impact of ion-bombardment. To this end, an alternative etching process based on the modification of silicon nitride by light ions followed by the selective removal of the modified layers by DHF has already been reported [1]. However, this process uses non-compatible etch techniques (dry and wet etch). To overcome this challenge, we have developed a plasma-based alternative to DHF. After the spacer etch, isotropic etching of silicon with infinite selectivity to the nitride spacer and underlying oxide is required for mandrel pull. Current methods used to etch silicon involve the redeposition of etch by-products and bombardment by energetic ions. Therefore, these processes are not isotropic and result in footing and significant damage to the underlying material.

In this presentation, we will demonstrate the feasibility of our approach to etch silicon nitride spacer without any footing and corner rounding. In addition, damage to the underlying oxide is negligible. We will also discuss the effects of non-idealities such as scattering and deflection of ions during the hydrogen plasma treatment and the incoming topographical defect on the etch profile. In addition, we will demonstrate the feasibility of novel strategies for isotropic etching of silicon with infinite selectivity to oxide, nitride, and other materials. These processes are by-product free and we do observe any footing. In addition, damage to the underlying material is negligible.

1. N. Posseme,O. Pollet, and S. Barnola, Appl. Phys. Lett., **105**, 051605 (2014).

8:40am **PS-MoM2 Enhancing Fin Retention in Low-K Spacer Etch Processes Using a Highly Selective Etch Chemistry**, *N.P. Marchack,* IBM Research Division, T.J. Watson Research Center*; E. Miller,* IBM Research at Albany Nanotech*; R.L. Bruce, H. Miyazoe, E.M. Sikorski,* ***Sebastian Engelmann,*** *E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; S. Kanakasabapathy,* IBM Research at Albany Nanotech

Low-k spacer materials such as SiBCN have garnered attention recently for advanced technology nodes due to their controllable electrical conductivity, low thermal expansion coefficient and potential for reducing loading capacitance. [1] Of particular concern in a spacer etch process is reducing the damage caused to materials such as the bottom oxide (BOX) and the underlying fins in FinFET systems. This is often a difficult challenge owing to the tight pitches and widely disparate critical dimensions (CDs) between the fin and gate geometries.

We present a spacer etch process using a novel high-selectivity gas chemistry that shows minimal damage in a FinFET system with SiBCN spacer deposited over SiGe fins. In addition to reduced damage compared to a conventional CH_3F/O_2 plasma chemistry, we also demonstrate greatly improved throughput even at low duty cycles by taking advantage of the unique chemical properties of the gas. We show <5nm SiGe fin loss for long overetch values, with minimal box loss as measured by high-resolution transmission electron microscopy (TEM).

The effect of pulsed plasma parameters are analyzed via optical emission spectroscopy (OES) in an attempt to define the etching mechanisms, as well as explain the difference between blanket etch conditions and patterned features. We focus on the effect of He dilution within the plasma as well as the effect of phase difference between source and bias for synchronous pulsing cases.

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9:00am **PS-MoM3 Effect of the Amount of Hydrogen During SiN etching on Etching Properties**, ***Nobuyuki Kuboi***, *H. Minari, M. Fukasawa, Y. Zaizen, J. Komachi, T. Kawamura, T. Tatsumi,* Sony Corporation, Japan

Silicon nitride (SiN) is an essential film in complementary metal oxide semiconductor devices. The amount of hydrogen contained in SiN films depends on the process conditions used in chemical vapor deposition (CVD), and strongly affects the etching properties of etching rate (*ER*), C-F polymer thickness ($T_{C\text{-}F}$), and damage. Therefore, revealing the mechanism of how hydrogen influences etching is very important to predict and control damage distribution considering the etching profile, and to develop etching processes with high selectivity for SiN over SiO_2.

To model SiN etching under the effect of hydrogen, we performed experiments using a dual-frequency capacitively coupled plasma system. We prepared three kinds of SiN_x:H_y films with y = 2.6%, 16.8%, and 21.9% (denoted as LP-SiN, Low-H SiN, and High-H SiN, respectively) on Si substrates using different CVD processes. The films were treated with CH_2F_2/O_2/Ar plasma under a gas pressure of 20 mTorr and Vpp of 350 V, for which we measured *ER* and $T_{C\text{-}F}$ values. We also measured plasma and surface conditions using various monitoring techniques. We analyzed the results through a first-principles calculation with VASP [1].

We found that for the low $CH_2F_2/(CH_2F_2+O_2)$ ratio where few C-F polymer layers existed, the *ER* values of High-H SiN were 20%–40% smaller than those of LP-SiN and Low-H SiN. In contract, inverse behavior was observed in the case of a high $CH_2F_2/(CH_2F_2+O_2)$ ratio. Considering variation of OES data and reactivity estimated by the VASP calculation, under the assumption that the etching front consisted of two layers (C-F polymer layer and reactive layer) [2], not only reaction between the outflux of H from the reactive layer and F from plasma but also termination of Si dangling bonds by H seems to cause variation of the *ER* value when the $CH_2F_2/(CH_2F_2+O_2)$ ratio is low. Because a C-F polymer layer of moderate thickness existed over the reactive layer at high $CH_2F_2/(CH_2F_2+O_2)$ ratio, some H was consumed by reaction with C in the polymer layer, which weakened the effects of H such as deactivation of F and termination of Si dangling bonds. This seems to lead to the inverse behavior observed at high $CH_2F_2/(CH_2F_2+O_2)$ ratio.

We formulate the above effect of H and include it in our SiN surface reaction model using the 3D voxel-slab method [3], reproducing *ER* and $T_{C\text{-}F}$ values. We also demonstrate SiN side-wall etching of fin-type field-effect transistors and discuss how to control etching profile and damage distribution.

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9:20am **PS-MoM4 Dual Channel Si/SiGe Fin patterning for 10nm Node and Beyond**, ***Fee Li Lie***, *E. Miller, P. Xu, S. Sieg, M. Sankarapandian,* IBM Research*; S. Schmitz, P. Friddle,* Lam Research Corporation*; G. Karve, J. Strane,* IBM Research*; K.Y. Lim, K. Akarvardar, M.G. Sung,* GLOBALFOUNDRIES, Inc.*; S. Kanakabasapathy,* IBM Research

As geometric scaling of silicon CMOS technology reaches its limits, continued device performance enhancement requires innovative approaches such as alternative channel materials. Owing to its relatively high hole mobility, much attention has been given to SiGe as a candidate for PFET channel material. The introduction of Ge in the material system affects the vertical and lateral etch behavior of the system depending on the Ge%. Typical balancing act of sidewall passivation and etch to yield vertical and on-target critical dimension (CD) fins now needs to be done on both Si and SiGe simultaneously. Furthermore, subsequent dry/wet clean processes, which generally does not impact Si fins, also interacts with SiGe fin and affects the final fin profile and CD. In this paper, we will present key challenges and approaches pertaining to etching dual channel Si/SiGe fin and subsequent dry/wet clean processes.

9:40am **PS-MoM5 Computational Patterning and Process Emulation: Linchpins to Enable Continued Scaling through Design Technology Co-optimization for Advanced Nodes**, ***Derren Dunn***, IBM Corporation **INVITED**

Enabling continued scaling at a pace that meets market demands will require new paradigms to define and evaluate early hardware design guidelines. Increasingly, patterning process implementations will be key factors in defining the boundaries of design spaces available for nodes beyond 10 nm. Self aligned patterning approaches will enable design spaces with significantly different entitlements than direct print patterning strategies due to process control dependencies, complexity, and physical process limitations. Identifying early design guidelines through process simulation and emulation that incorporate a full range of patterning processes required for a given front end of line (FEOL) approach will be key to delivering nodes on time. These processes will undoubtedly include lithography, reactive ion etch, spacer deposition, and wet clean processes. In addition, EUV solutions will require accurate estimates of line width variation, line end pull-back, and new materials challenges that will influence early design decisions. In this talk, we will demonstrate how coupling advanced process simulation with process emulation can be used to evaluate early FEOL design guidelines and establish criteria for equipment and materials vendors. We will also suggest approaches to establishing design entitlement metrics for typical FEOL self aligned patterning processes and EUV direct print approaches that might be used in future gate and fin process modules.

10:40am **PS-MoM8 Overcoming Challenges of sub-10NM FinFET Gate Etching in Halogenated Plasmas.**, ***Sergey Voronin***, TEL Technology Center, America, LLC*; J.R. Sporre, S. Kanakasabapathy,* International Business Machines – Research Division*; A. Ranjan,* TEL Technology Center, America, LLC

Moore's law extension in the semiconductor industry requires processing of features at nanometer scale. Approaching sub-10NM technological fabrication we face more stringent requirements to the etch process (high anisotropy and high selectivity to the mask films).

We present peculiarities and new challenges of 3D gate etch processing in halogen-based plasmas. These include by-product -free etching of narrow features, "FIN-Gate" corner residue removal, prevention of merging of the neighboring gates and advanced selectivity control to the FIN oxide. To combine all these in one process, we need multiple unique steps responsible for certain stages of etching. The etching mechanisms and dependence of the etching properties (selectivity, anisotropy and etch rate) on the plasma discharge parameters (electron temperature, ion and radical densities, ion energy) will be described for each step. We have successfully approached the 7NM technological node at aspect ratios and, etch depths up to 6:1 and 160 nm, respectively, with a potential for the next technological generation.

An additional subject of discussion is related to surface-plasma interactions between charged and neutral species in HBr plasmas. Formation and deposition of non-volatile bromine-containing by-products $SiBr_x$ (x=1,2) and $SiBr_xO_y$ can result in clogging of narrow features, etch profile distortion, limited etching depth and residual Si at high aspect ratios. These non-volatile species are accumulated on the process chamber wall, desorb to the gas phase and can re-deposit on the processed wafer for long times – well after the main etch process is over. We demonstrate the importance of the chamber wall chemistry condition and plasma discharge parameters in formation and re-deposition of these species. Chamber wall surface cleaning by fluorine-containing plasmas and lowering the source power resulted in significantly smaller amounts of by-product and can be used as profile control knobs in the process.

11:00am **PS-MoM9 Gate Etch Challenges Introduced by FinFET Gate Pitch Scaling**, ***John Sporre***, IBM Research Division*; X. Liu,* IBM Research Division, T.J. Watson Research Center*; S. Seo,* IBM Research Division*; C. Prindle,* GLOBALFOUNDRIES, Inc.*; P. Montanini,* IBM Research Division*; R. Xie,* GLOBALFOUNDRIES, Inc.*; M. Sankarapandian, S. Mehta, M. Breton, S. McDermott, S. Kanakasabapathy,* IBM Research Division*; B. Haran,* IBM Research

Continued scaling of FinFET technology introduces unique challenges with respect to patterning high aspect ratio structures. In addition to the traditional challenge of etching a gate with uniform sidewall and cross wafer uniformity, new challenges are introduced as a result of the reduction of inter-gate spacing. Maintaining selectivity to dielectrics during Si etch can result in profile degradation due to etch polymer by-product pinch-off. Low polymer producing chemistries can prevent this pinch-off, but with the cost of unacceptable Fin erosion. Furthermore, gate profile and pitch control can have significant impact on down stream process stability and may result in downstream gate bending. In this paper, the unique challenges caused by gate pitch scaling will be explored with respect to not only their impact on downstream functionality, but also to the gate etch itself.

11:20am **PS-MoM10 Hybrid Fin reveal for tight Fin Pitch Technologies**, ***Peng Xu***, IBM Research Division; *P. Wang,* Lam Research Corporation; *Z.X. Bi,* IBM Semiconductor Technology Research; *T. Devarajan,* IBM Research Division; *B. Nagabhirava, A. Basavalingappa,* Lam Research Corporation; *F.L. Lie, J. Strane, M. Sankarapandian, S. Mehta, R. Conti,* IBM Research Division; *M. Goss,* LAM Research Corporation; *D. Canaperi, D. Guo, S. Kanakasabapathy,* IBM Research Division

FinFET based CMOS technologies continue scaling down in Fin Pitch1-3. Self-aligned double patterning (SADP) and Self-aligned quadruple patterning (SAQP) have been used to form tight Fin pitch structure. Device requirements and layout constraints can result in the need to cut different numbers of fins, which form variable spaces between fins, but a consistent Fin height must be maintained. In addition to the space variability, gap fill oxide density variations are observed depending on local feature density. A key process for defining the height of the active fin for Bulk Substrates is the Fin reveal process

Such space and film density variations between Fins introduce significant challenges for the Fin reveal process, especially in the sub 40nm Fin pitch range. In this paper, we show initial results from a hybrid Fin reveal process, that combines anisotropic etching with reactive clean techniques. We show the ability to maintain fin reveal depth uniform across feature densities and quality.

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11:40am **PS-MoM11 Damage Free Plasma Etching Processes for the Patterning of InGaAs fin for the sub-10nm Technological Node**, ***Maxime Bizouerne***, *E. Pargon,* LTM, Univ. Grenoble Alpes, CEA-LETI, France; *P. Burtin,* CEA, LETI, MINATEC Campus, France; *C. Petit-Etienne, E. Latu-Romain, S. Labau, M. Martin,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The conventional Si CMOS technology recently encounters difficulties to maintain its dimensional scaling owing to the high power consumption of logic chips. The planar MOSFET has already evolved to a FinFET, a three dimensional device architecture which provides lower leakage current. New channel materials are now therefore considered to continue the transistor scaling and enable higher device densities with faster logic switching and lower power consumption. The III-V semiconductors which present electron velocities ten times higher than the silicon, are seriously considered as N-channel materials in a FinFET architecture for the sub-10nm technological node. To complete this integration, the development of plasma etching processes dedicated to the III-V fin patterning is necessary. The major challenge for nanometer-scale III-V finFET definition by plasma etching is the realization of vertical sidewalls with a high quality surface.

In this work, we address this challenge by undertaking a systematic investigation of dry etch processing for InGaAs fin formation, with the aim of obtaining high resolution fins with vertical sidewalls and clean etch surfaces. The InGaAs layers have been grown by MOCVD on 200mm Si wafer and photoresist lines with dimensions ranging from 20 to 100nm have been patterned by ebeam lithography. The plasma etching experiments are carried out on a 200mm etching platform from AMAT composed of two inductive coupled plasma reactors, whose one is equipped with a hot cathode. The performance of Cl_2 and CH_4 based plasma processes at 50°C and 200°C have been evaluated and compared in terms of anisotropy, surface roughness and plasma induced chemical damages. A particular attention is paid on the chemical and physical damages induced on the pattern sidewalls. The pattern profiles are characterized by electron microscopies. The sidewalls roughness is measured by AFM using a homemade setup where the sample is tilted to allow the tip to scan the sidewalls. The sidewalls chemical composition and stoichiometry after etching is analyzed by nanoauger spectroscopy. We also investigate restoring processes to mitigate the etch-induced sidewalls damages by combining oxidation and wet removal steps. Finally, we propose a new method to pattern the III-V fins without generating etching damages. It consists of a two-step process, starting with a surface modification by a He or H_2 plasma implantation followed by a wet cleaning to remove the modified surface without damaging the non-modified one. This method appears promising to etch the III-V fin without damaging the fin sidewalls and will be benchmarked to conventional plasma technique.

Plasma Processing for Biomedical Applications Focus Topic
Room 101A - Session PB+BI+PS-MoA

Plasma Processing of Biomaterials

Moderators: Denis Dowling, University College Dublin, Deborah O'Connell, University of York, UK

2:00pm **PB+BI+PS-MoA2 Atmospheric Plasma Deposition of Antimicrobial Nano-Coatings on Biomedical Textiles**, *A. Nikiforov, I. Kuchakova, T. Coenye, C. Leys,* Ghent University, Belgium*; N. Hojnik, M. Modic,* ***Uroš Cvelbar,*** Jozef Stefan Institute, Slovenia

In this work, the antimicrobial non-woven fabrics were prepared with the use of atmospheric pressure plasma deposition.Atmospheric pressure DC jet operating in N_2 at current density of 6 mA/cm^2 and voltage of 15 kV is used as a source of non-thermal plasma for engineering of the antibacterial nano-composites on surface of polymeric polyethylene terephthalate (PET) meshes. Nano-particles of Ag, Cu and ZnO are tested as antimicrobial agents through incorporation in to the structure of the plasma deposited composite film. The deposition process is carried out in three steps process. The fabric is first pretreated by depositing a first layer (250 nm - 500 nm) of organosilicon thin film using an atmospheric pressure plasma system, then nano-particles are incorporated by a dipping-dry, and finally the nano-particles are covered by a second organosilicon layer of 10-50 nm thickness. Top layer in the composite coating of “sandwich-like structure” with variable thickness is used for precise control of metal ions release and so to tune antimicrobial efficiency of the material. The deposition process and surface chemistry of the coatings are studied by emission spectroscopy, and surface analysis techniques: XPS, AFM and SEM. The antimicrobial activity of the treated fabrics is also tested against *Pseudomonas aeruginosa* and *Staphylococcus aureus*. It is revealed that thickness of top (barrier) layer plays a key role in release of metal ions and negligible small antibacterial activity is observed if barrier thickness exceeds 50 nm. Tests with *S. aureus* show that the highest 98% bacterial reduction is achieved with Cu NPs whereas Ag NPs are much less effective and can provide only 79% reduction. In contrast, the fabric antibacterial efficiency against of *Pseudomonas aeruginosa* is very low for both Cu and ZnO nanoparticles in spite of the load and only Ag NPs are proved to be effective (2 orders reduction) against of *P. Aeruginosa*. The results clearly indicate that plasma of atmospheric pressure can be used as effective tool for immobilization of nano-particles in composite coatings. Control of antibacterial activity can be achieved through variation of deposition parameters and a type of incorporate nanoparticles. The approach might present a new route to preparation of effective antimicrobial materials against of certain class of bacteria.

This work is partially supported by the M.Era-Net project “PlasmaTex”.

2:20pm **PB+BI+PS-MoA3 Plasma Polymers for Biomedical Applications**, ***Farzaneh Arefi-Khonsari,*** l'université Pierre et Marie Curie, France*; A. Baitukha, J. Pulpytel, A. Valinataj Omran,* Sorbonne Universités, UPMC, France **INVITED**

In this talk, different nonequilibrium atmospheric pressure plasmas used for biomedical applications such as planar DBD, single and double barrier DBD plasma jets, and transported discharges in tubes will be discussed. Indeed in the case of the latter, deposition and surface treatment, by means of a He cold transported discharge in tubes as long as 200 cm and tube inner diameters ranging from 1 to 20 mm, can present a great potential for surface modification of polymers used as biomaterials. We have, as well as several research groups, succeeded to retain the precursor moieties to obtain PEG like polymers which present interesting antifouling properties by using planar DBD and jets. However for particular plasma applications such as making a Drug Delivery System (DDS) based on several polymer or copolymer layers, encapsulating the drug, it is more reasonable to use a low pressure plasma which can give rise to dense crosslinked barrier films. The latter are less flexible and develop microcracks due to swelling and curvature of the host biocompatible and biodegradable substrate. In order to obtain good cohesive coatings with excellent barrier and mechanical properties, it is very important to deposit layers presenting a vertical chemical gradient, where stress is gradually distributed over the rigid and flexible zones of the DDS, which is more easily deposited in low pressure plasmas. Our recent results in copolymerizing amphiphilic precursors for the use of cell adhesive or nonadhesive surfaces will be presented. Such copolymers can be also used as biodegradable multi-layer copolymers for drug delivery applications. Human ovarian carcinoma cell lines (NIH:OVCAR–3) were used for *in vitro* measurements of cell interactions with the surface of fabricated DDS. Proposed model of DDS on collagen films prevents migration, adhesion and growth of cancer cells on its surface, and by tuning the thickness of the dense barrier films, encapsulating the drug, it is possible to control the drug release kinetics and to improve the therapeutic effect. *In vivo* experiments were carried out by injecting OVCAR3 cells in mice lymph nodes to develop a tumor, followed by implantation of the DDS membranes to evaluate the feasibility of the proposed model.

3:00pm **PB+BI+PS-MoA5 Plasma Coating Using Biologics: Degradation or Polymerisation?**, ***Liam O'Neill,*** *J. O'Donoghue,* TheraDep, Ireland **INVITED**

The interaction of plasma with biomolecules is generally viewed as being a simple degradation reaction in which the plasma denatures any biologic material it encounters. Using a combination of heat, UV, free radicals, electrons and ions from the plasma, it is possible to cut, oxidise, burn and even ablate biological materials and this has established plasma sterilisation as a trusted technique in science, medicine and engineering.

However, recent research in our labs has shown that it is possible to minimise these effects and to instead use the plasma to cross-link biologic materials with retention of the biological properties of the precursor materials. Using low levels of applied plasma power, it is possible to produce low energy helium and argon plasma discharges. When biomolecules are nebulised into such a low temperature plasma, the materials are activated without losing their chemical structure. This activation can then effectively cross-link or coagulate the biomolecule without significant degradation. In addition, the plasma can activate substrates and effectively bind the biomolecules to the substrate as a thin nano-scale coating.

The result is a one-step process capable of modifying the surface of medical devices, research and diagnostic lab ware, implants and even living tissue. Tailored biological surfaces can be grown in situ over large areas using established equipment systems. The mechanisms used to control such reactions and to move the plasma from degradation to cross-linking modes are now being established and will be discussed. Examples of protein and polysaccharide coatings produced to date will also be presented.

4:00pm **PB+BI+PS-MoA8 Low and Atmospheric Pressure Plasma Polymerization for Immunosensing and Tissue Engineering**, ***Lenka Zajickova,*** *A. Manakhov, E. Makhneva, J. Medalova, D. Necas,* Masaryk University, Czech Republic*; L. Strbkova,* Brno University of Technology, Czech Republic*; A. Obrusnik, M. Landova,* Masaryk University, Czech Republic **INVITED**

Plasma polymerization provides a large playground for the preparation of surfaces suitable for immobilization of biomolecules and colonization by cells because chemical, structural and functional properties of plasma polymerized thin films can be tuned accordingly. The key decision for the particular application is the selection of functional chemical group that the final plasma polymer should contain. This contribution is going to discuss deposition of plasma polymers containing amine and carboxyl groups, functional groups that are typically used in biochemical applications and that are proposed to influence positively the attachment and proliferation of cells at surfaces. Amine-rich films were deposited in the low pressure pulsed radio frequency discharge using vapors of cyclopropylamine mixed with argon. The films contained primary and secondary amines and a small amount of oxygen. The structure of the films, reflected in their stability in water, could be tuned by the plasma conditions. The relationship between the amount of amine groups and the water stability was not straitforward because the films with similar amount of primary amine groups but different cross-linking could be prepared. The plasma polymers containing anhydride groups that hydrolyzed fastly at air into carboxyl groups were deposited in kHz-frequency dielectric barrier discharge at atmospheric pressure from the mixture of maleic anhydride and acetylene. The variation of the flow rate ratio was used to optimize the stability of films together with the amount of functional groups. Amine and carboxyl plasma polymers proved to be useful for the preparation of immunosensors based either on the principle of quartz crystal microbalance or surface plasmon resonance because in both these methods it is necessary to prepare a stable and reactive film on the gold surface. The amine films were also tested for the cultivation of human dermal fibroblasts and mouse myoblasts. It was identified that the water stability of the films is very important for succesfull experiments

4:40pm **PB+BI+PS-MoA10 Low-Temperature Plasma Processing of Polymeric Materials for Biomedical Applications**, ***Michelle Mann***, *M.R. Maynard, E.R. Fisher,* Colorado State University

Polymeric biomaterials are widely used in medical applications such as wound healing, drug release, and blood dialysis. For example, Tygon® and similar thermoplastics are chosen for these applications because of excellent mechanical strength and flexibility but often suffer from bacterial attachment and proliferation that ultimately leads to infection and fouling of the biomedical device. Biocidal agents can be incorporated into the polymer to actively eradicate bacteria, but it is difficult to ensure that biocidal action is localized at the material-biological interface. As a result, changing the surface properties of the polymer ensures a second mechanism by which to discourage bacterial attachment and growth. Plasmas are frequently used to alter the surfaces of biomaterials, most often by surface modification or deposition of a film to discourage bacterial attachment, while retaining the bulk properties critical to device performance. Specifically, H_2O (v) plasma treatment can enhance the compatibility of biomaterials by increasing hydrophilicity and altering surface chemistry; here, we demonstrate the use of this treatment method specifically for antibacterial materials. First, we have used H_2O (v) plasmas to tune the release of an antibacterial agent (NO) from drug-releasing polymers. Composition of treated drug-releasing polymers measured via X-ray photoelectron spectroscopy demonstrates a 100% increase in oxygen content and an associated increase in wettability, as observed via water contact angle goniometry. Compared to the untreated polymer, H_2O (v) plasma treated polymers had a delayed, but equally dramatic 8-log reduction in growth of both gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus*. Second, in a related study, we utilized plasma-enhanced chemical vapor deposition to deposit a film of 1,8-cineole, an antibacterial constituent of tea tree oil. Bacterial attachment and biofilm formation assays reveal significantly reduced growth of both bacterial strains on plasma polymerized cineole films. H_2O (v) plasma treatment of these materials will also be discussed. Furthermore, optical emission spectroscopy allows correlation of gas phase excited state species in our plasmas under various plasma conditions to the resulting 1,8-cineole film surface properties, thereby allowing for fine-tuning of film surface properties for deposition onto biomedically-relevant polymer structures such as 3D polycaprolactone scaffolds. Collectively, our studies of plasma processing of antibacterial materials demonstrate this technique is a valuable tool in the production of next generation biomedical devices.

5:00pm **PB+BI+PS-MoA11 Plasma-based Functionalization of Polystyrene Surfaces of Cell Culture Plates**, ***Kazuma Nishiyama***, *T. Ito, S. Sugimoto, K. Gotoh, M. Isobe,* Osaka University, Japan*; M. Okamoto,* Osaka University Hospital, Japan*; A. Myoui,* Osaka University Hospital, Japanl*; H. Yoshikawa, S. Hamaguchi,* Osaka University, Japan

Polystyrene is one of the most widely used cell-culture plate materials. Amino and/or carboxyl coated cell culture plates are commercially available and such surface functionalizations are known to contribute effectively to the control of growth and differentiation of various stem cells. Plasma-enhanced chemical vapor deposition (PECVD) or plasma ion implantation may be used to functionalize polystyrene surfaces of cell culture dishes. The goal of this research is to understand how such surface functionalizations are affected by plasma conditions. In this study, we have used molecular dynamics (MD) simulation to understand how incident ions and free radicals affect the formation of amines and carboxyl groups. The simulation is based on interatomic reactive potential functions developed in-house based on quantum mechanical calculations. Results of MD simulations under the conditions similar to PE-CVD by ammonia (NH3), cyclopropylamine (CPA), or N2/CH3OH plasmas or ion implantation by NH3, N2/H2, or N2/CH3OH plasmas suggest that, with energetic ion bombardment, functional groups such as primary amines are less likely to form and nitridation of the surface tends to occur. Some simulation results have been compared with experimental data obtained from parallel-plate discharges with an inverter power supply at a relatively high gas pressure of 250 - 2,500 Pa and found to be in good quantitative agreement.

Plasma Science and Technology
Room 104D - Session PS+AS+SS-MoA

Plasma Surface Interactions

Moderator: Richard van de Sanden, FOM Institute DIFFER, Netherlands

1:40pm **PS+AS+SS-MoA1 Atomic-scale Analyses of Plasma Etching for Unconventional Materials in Microelectronics**, ***Satoshi Hamaguchi***, *K. Karahashi,* Osaka University, Japan **INVITED**

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven invention of new device technologies such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this study, we shall review our recent work on analyses of etching selectivity and surface chemical reactions for magnetic materials [1,2] metal oxides[3,4], Si-based materials [4] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes. In our analyses, we use multi-beam injection experiments [8] and molecular dynamics (MD) simulations to emulate elementary processes of plasma-surface interactions that take place in RIE processes.

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2:20pm **PS+AS+SS-MoA3 Plasma Wall Interactions: Y_2O_3 Wall Interaction in Cl_2 Plasma Etching of Si and NF_3 Plasma Cleaning**, ***Tianyu Ma***, *T. List, V.M. Donnelly,* University of Houston

The walls of a plasma etching chamber play a critical role in causing variability of processing metrics such as rate, profile shape and selectivity. Small changes in the nature of the chamber wall surfaces can affect radicals sticking coefficients, recombination probabilities, and other heterogeneous reactions that will cause changes in the number densities of species in the plasma, which in turn affects the process. Therefore, a stable chamber wall material is essential for plasma processes, and in particular plasma etching. Compared to traditional alumina and silica wall material, Y_2O_3 has high chemical stability and extending lifetime, making it one of the preferred wall materials in etching systems. Consequently, studies were performed in a chamber with Y_2O_3-coated walls to determine time-dependent variations in the number densities of species in inductively coupled Cl_2/Ar and NF_3/Ar plasmas. Si was etched in Cl_2 plasmas, after which, the wafer was removed and an NF_3 plasma was used to remove etching products that deposited on the walls. This etch-clean procedure was repeated many times, simulating an integrated circuit manufacturing etch process. Optical emission spectroscopy (OES) and Langmuir probe analysis were performed to characterize plasma. Y_2O_3-coated coupon pieces exposed to the plasma were examined by X-ray photoelectron spectroscopy (XPS). Number densities of Cl_2, Cl, O, and F were obtained with rare-gas actinometry during the entire etching and cleaning cycles. Emissions from Si, SiCl, $SiCl_2$, $SiCl_3$, SiF, and N_2 were also recorded. After exposure to the NF_3 plasma, Cl number densities are relatively low when no substrate bias is placed on the

Si substrate. As soon as bias is initiated, Cl number density rises steeply at first and then slowly maximizes. This is attributed to then displacement of F on the walls with a $SiCl_x$ containing layer. Apparently Cl on its own cannot remove F efficiently, but the reaction of Si-containing etching products produces SiF surface species that desorb and are observed as transient SiF emission in the first moments of etching. Cl recombination on this surface is much lower than on the fluorinated Y_2O_3 surface. Once prepared by etching Si with bias, the Cl number density remains high if bias is extinguished and etching nearly stops. The higher recombination coefficient on fluorinated surfaces is attributed to the longer residence time of physisorbed Cl, caused by the attraction to positively charged Y sites that are created when Y forms mainly ionic bonds with F.

2:40pm **PS+AS+SS-MoA4 Novel atomic order CD Control Technology by Fusion of Quasi-ALE and ALD**, ***Yoshihide Kihara***, *T. Hisamatsu,* Tokyo Electron Miyagi Limited, Japan*; T. Oishi, S. Ogawa, H. Watanabe,* Tokyo Electron Miyagi Limited*; A. Tsuji, M. Honda,* Tokyo Electron Miyagi Limited, Japan

In the recent years continuous scaling has required the use of multiple mask patterning technologies such as double and quadruple patterning, and increasingly thin EUV mask films are being planned to be used in the near future. In the patterning process, the fabrication of multilayer films requires the precision of atomic layer level accuracy (within nm level). Some critical challenges that patterning schemes face includes thinning of mask materials, reduction of ARDE related CD-loading, and reduction of LER and LWR. This requires the realization of highly selective etch processes that can address the challenges without trade-offs in other process specifications.

One method to increase the mask selectivity to enable mask thinning, which is one of the major patterning issues, Si-ARC is etched in a depositing condition which protects the resist mask surface, utilizing the material difference between the mask material and the antireflective layer (Si-ARC). However, to enhance selectivity, extra amount of the deposition can be generated. The amount of deposition flux fluctuates depending on the pattern density, leading to CD loading. In order to solve the tradeoff between selectivity and loading, we have proposed a Quasi- Atomic Layer Etching (Quasi-ALE) which is a modification of ALE to employ thin-film adsorption and activation by low ion energy [1]. In this paper, Quasi-ALE is applied to Si-ARC etch step to address three challenges; high selectivity, pattern-independent CD-loading, and vertical etch profiles.

We have also proposed the combination of ALD with etch as CD-loading-free CD control technique [2]. By combining ALD and Quasi-ALE, excellent CD controllability was achieved to address the entire patterning process issues without tradeoffs. In the presentation, various merits of the Fusion Process, which is a combination of Quasi-ALE and ALD, in patterning process, will be introduced. Fusion Process has a significant potential to solve critical challenges in the patterning process of N7, N5 and beyond.

Reference

[1] A.Tsuji et al., AVS 62nd Int. Symp. (2015)

[2] T.Hisamatsu et al., AVS 62nd Int. Symp. (2015)

3:00pm **PS+AS+SS-MoA5 Development of a New Analysis Technique of Nanostructures Etched by Plasmas: Quasi In-Situ TEM EDX Characterization**, ***Matthieu Serege,*** LTM, Univ. Grenoble Alpes, CEA-LETI*; G. Cunge,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; L. Vallier, E. Latu-Romain,* LTM, Univ. Grenoble Alpes, CEA-LETI*; O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

As the size of integrated circuit continues to shrink, plasma processes are more and more challenged and show limitations to etch nanometer size features in complex stacks of thin layers. The achievement of anisotropic etching relies on the formation of passivation layers on the sidewalls of the etched features which act like a protective film that prevents lateral etching by the plasma radicals. However, this layer also generate a slope in the etch profile and it's difficult to control the layer thickness. Another thin layer called "reactive layer" is also formed at the bottom of the feature where the energetic ion impact mix the material to be etched with the plasma radicals. Etch products are formed allowing a high etch rate of the silicon substrate. It starts to be realized that controlling the thickness of this reactive layer is the key to achieve very high selective processes. Indeed, accurate etch stop on an ultra-thin layer is only possible if the thickness of this stop layer is higher than the thickness of the reactive layer otherwise damages are created underneath the stop layer.

A better understanding of these layers chemical nature, thickness and deposition mechanism is mandatory, but the main problem is that the layers to be analyzed are chemically highly reactive because they contain large concentrations of halogens and they get immediately modified (oxidized) when exposed to ambient atmosphere.

In this work we develop an original, simple and extremely powerful approach to observe passivation layers quasi in-situ (i.e. without air exposure): After plasma etching, the wafer is transported *under vacuum* inside an adapted suitcase to a deposition chamber where it is encapsulated by a metallic layer (magnetron sputtering PVD). Then, the encapsulated features can be observed ex situ without chemical / thickness modification using FIB-SEM (specimen preparation) coupled with a TEM-EDX analysis: HRTEM observation provides an extremely precise measurement of the passivation layer and encapsulation morphology. In parallel, STEM-EDX is used to map the main atomic element in our specimen, supplying qualitative information on the layer chemical composition. STEM-EDX is also used in profile mode to give us more accurate quantitative analysis. We are able to estimate the (relative) quantitative atomic concentration along a line scan profile on the feature sidewalls.

The measurements relatively fast, provide accurate analysis at the nanoscale, and are highly promising to better understand plasma etching processes. Therefore, this technique will be very helpful to develop innovative processes controlled at the nanometer range.

3:20pm **PS+AS+SS-MoA6 Atomistic Simulations of He Plasma Modification of Si/SiN Thin-Films for Advanced Etch Processes**, ***Vahagn Martirosyan,*** LTM, Univ. Grenoble Alpes, CEA-LETI, France*; E. Despiau-Pujo,* CNRS - LTM, France*; O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous

wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the

active layers of advanced nanoelectronic devices (e.g. FDSOIs, FinFETs). In particular, silicon nitride

or low-k spacers etching must be performed with nanoscale-precision without creating defects to the

underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To

solve this problem, one possible alternative is to use a recently developed etch technology, which

consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H 2) or

helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet

cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the development of such a new etch approach

requires a more detailed understanding of the fundamental mechanisms involved in the process.

Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-He and Si-N- He systems

and provide an overview of the reaction processes at the atomic scale. The objective is to understand

precisely the role of ion energy in the self-limited ion implantation, and to determine the relationship

between the flux/energy of plasma species (He +) bombarding the surface and its structural/chemical

modifications.

In this work, we investigate the interaction between helium plasma species (He+ ions) and

silicon/silicon nitride via MD simulations, by studying the influence of ion energy (5-100eV) and ion

dose on the substrate modification. For He/Si interactions, simulations show an initial He implantation

followed by the formation of a stable modified layer at steady state, composed of two parts: a Si-He

mixed amorphous layer and a thin sublayer, which is crystalline but enriched in helium. According to

our results, the higher is the ion energy, the more rapid is the contamination and the thicker is the

amorphous layer. Few or no Si sputtering is observed for energies lower than 100eV, confirming that

He plasmas can modify/weaken the material on a precise depth without etching it. Amorphisation of

the material leads to the rupture of crystalline Si-Si bonds and to the creation of a less dense modified

layer, facilitating its subsequent removal by wet or dry etching. Mechanisms of helium

retention/desorption, as well as comparisons between He/Si and He/SiN interactions, will be

discussed during the presentation.

References

1. N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

4:20pm **PS+AS+SS-MoA9 Patterned Chromium Hard Mask Etching in a Two Reactant Gas for Bit Patterned Media Template Fabrication***, **Daniel Staaks**[*], *Molecular Foundry, Lawrence Berkeley National Lab*; *X. Yang,* Seagate Technology*; S. Dallorto, S.D. Dhuey, S. Sassolini,* Molecular Foundry, Lawrence Berkeley National Lab*; K.Y. Lee,* Seagate Technology*; I.W. Rangelow,* Ilmenau University of Technology, Germany*; D.L. Olynick,* Molecular Foundry, Lawrence Berkeley National Lab

Plasma-based dry etching is one of the most important nanofabrication methods for transferring full-wafer patterns. As feature sizes approach the single digit nanometer regime, there is an urgent need to develop a comprehensive and detailed understanding of the associated etching mechanisms. Additionally, challenges in obtaining high anisotropy, high selectivity, and robust critical dimension control must be addressed.

Highly selective chromium etching masks are an area of particular interest. Chromium has a widespread utility in not only manufacturing photolithography masks, but also in fabricating high-resolution nanoimprint templates. For example, we use it as a highly selective hard mask when etching SiO2 to achieve Bit Patterned Media templates towards sub-5nm features (7Tb/in²).

To date, there have been few investigations into patterned chromium films. The limited studies available involve micron-sized features and patterning by the erosion of polymer masks, which make extrapolation to the single-digit nano regime very difficult. In this work, we bridge the gap for nanoscale-patterned films. We etch a patterned 20nm layer of chromium in low pressure and low power Cl_2/O_2 plasmas. We investigate the profile evolution of features ranging from 15nm- to 200nm in pitch. Previous work in etching blanket chromium films revealed that chromium etch rate was influenced by substrate temperature and Cl_2/O_2 flow [1]. Here, we vary percent O_2 flow (1%, 50%, 87%) and temperature (-50°C, +20°C) to explore the effects on lateral etching mechanisms, etch lag, and anisotropy. Using a highly selective HSQ mask for etching the chromium allows us to better determine the involved etching mechanisms. High-resolution micrographs of thin film cross-sections show significantly enhanced anisotropy at low temperatures.

Additionally, the unique etching chemistry of chromium must be considered when evaluating the material as a mask. Most materials form multiple volatile binary compounds during the etching process. Chromium, on the other hand, forms a single ternary compound: chromyl chloride. This enables us to study the effect of two-reactant gas chemistry on the etched feature profile. Results indicate that gas phase transport and surface mass transport of oxygen and chlorine are influential to profile shapes. Moreover, the effective local oxygen concentration inside the trench is important, and surface-dominated reactions highly affect the profile. Chlorine rich and chlorine poor chemistries promote very different surface reactions.

[1] D. Staaks, et al., Low temperature dry etching of chromium towards control at sub-5 nm dimensions, Nanotechnology 2016, submitted manuscript

4:40pm **PS+AS+SS-MoA10 Alternative Solutions for Nanometric-Precision Etching: H2 Plasmas Modification of Si/ SiN Thin-Films***, **Emilie Despiau-Pujo**, V. Martirosyan, O. Joubert,* LTM - CNRS/Univ Grenoble Alpes/CEA, France

Consisting of several ultrathin layered materials, advanced transistors (FDSOI, FinFET) must be etched with a nanometric precision and nearly infinite selectivity to preserve the electronic properties of active layers (e.g. the silicon channel), a challenge which cannot be addressed by conventional CW plasma processes. To achieve uniform and damage-free etching of multi-layered transistors, an alternative etch approach has been recently proposed, consisting in two steps. In a first step, the film to be etched is modified in volume by exposition to a hydrogen or helium conventional CCP or ICP; in a second step, the modified layer is selectively removed by wet cleaning or exposure to gaseous reactants only. Such a two-steps process showed promising results for silicon nitride spacers etching [1]. To assist the development of this new technique, Molecular Dynamics (MD) simulations - coupled to experiments - are used to investigate the interactions between H2 plasmas and Si/SiN films. These atomic-scale simulations aim at better understanding the relationship between the flux/energy of plasma species (Hx+ ions, H radicals) bombarding the surface and its structural/chemical modifications.

Although one material of interest is silicon nitride, the study of Si-H systems constitutes a first step to understand the impact of ion energy (5-100 eV) and ion dose on the substrate modification and self-limited ion implantation. Simulations of cumulative Hx+ (x=1-3) ion bombardment show a rapid hydrogenation of Si followed by the formation of a stable modified layer at steady state. This modified layer is composed of a thick amorphous Si-H mixed layer and a thin sublayer, quasi-crystalline but enriched in hydrogen. As hydrogen is highly chemically reactive, ion implantation leads to the rupture of crystalline Si-Si bonds and to the creation of SiH, SiH2, SiH3 covalent bonds in the modified material. At the bottom of the modified layer, hydrogen tends to saturate the dangling bonds of the amorphous silicon and to create SiH3 bonds, thus fracturing the substrate into a modified hydrogenated layer weakly bound to the underlying crystalline material (Smartcut-like mechanism). The influence of ion dose, ion energy and ion type on the modified layer thickness (and thus on the subsequent etch precision) are discussed. Comparisons between pure ion implantation and exposition to various H2 plasma conditions (simulated by bombarding the Si/SiN substrates with both Hx+ ions and H radicals) are also presented. [1] N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

5:00pm **PS+AS+SS-MoA11 Plasma Dynamics at the Surface Interface in Low Pressure Capacitively and Inductively Coupled Plasmas***, **Martin Blake**, D. O'Connell,* University of York, UK*; A.R. Gibson,* LPP, CNRS, Ecole Polytechnique, Université Paris-Saclay, France*; T. Gans,* University of York, UK

The plasma-surface interface in low temperature, low pressure plasmas used for industrial

wafer processing is difficult to characterise. However, understanding the plasma dynamics

at this interface is key for further optimisation of industrial plasma processes. Of particular

relevance are the densities of reactive species, such as atomic oxygen, in this region. In this

work a methodology has been developed based on newly augmented fast optical

techniques which can probe reactive species densities in the wafer region without the need

for expensive laser equipment. This technique, known as energy resolved actinometry

(ERA)[1], utilises phase resolved optical emission spectroscopy (PROES) measurements of the

direct and dissociative electron-impact excitation dynamics of three distinct emission lines,

750.4 nm (argon, added in small concentrations as a tracer gas) and 777.4 nm, 844.6 nm

(atomic oxygen). Through the ratio of the excitation functions and their energy dependence

we determine both the atomic oxygen density and the mean electron energy above the

[*] **Coburn & Winters Student Award Finalist**

electrode surface.

In this work ERA has been applied to measure atomic oxygen densities and local mean

electron energies in a low pressure (1 – 100 Pa) oxygen plasma produced in a GEC reference

cell system [2], operated at 13.56 MHz in both capacitive and inductive modes at power

inputs ranging from 50 – 500 W. Additional characterisation of the plasma-surface interface

is carried out through the use of a retarding field energy analyser (RFEA) to measure the ion

energy distribution at the surface. The combination of both approaches allows for

information on the neutral and ion dynamics in the surface region, both of which are known

to be important for process outcomes.

A two-dimensional hybrid plasma simulation code is used to simulate the same conditions in

order to improve understanding of the experimental results.

Acknowledgements:

This work has been supported through the UK Engineering and Physical Sciences Research

Council (EPSRC) manufacturing grant EP/K018388/1 and the authors would also like to thank

Intel Ireland, Ltd. for financial support.

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simultaneous measurement of atomic oxygen densities and local mean electron energies in

radio-frequency driven plasmas, Appl. Phys. Lett. 105 234105

[2] P. J. Hargis Jr et al (1994); The Gaseous Electronics Conference radio-frequency reference

cell: A defined parallel-plate radio-frequency system for experimental and theoretical

studies of plasma-processing discharges, Rev. Sci. Instrum. 65, 140

Plasma Science and Technology
Room 104B - Session PS-MoA

Advanced BEOL/Interconnect Etching

Moderator: Hisataka Hayashi, Toshiba, Japan

1:40pm **PS-MoA1 The Search for New Multi-Pattern Etch Colors: Usual (SiO_2, SiN, SiC) and Unusual (hi-k, BN, BC:H) Suspects**, ***Michelle Paquette***, *S. Dhungana, B.J. Nordell, A.N. Caruso,* University of Missouri-Kansas City*; W.A. Lanford,* University at Albany*; G. Chollon, C. Pallier, F. Teyssandier,* Universite de Bordeaux, France*; K. Scharfenberger, D. Jacob, S.W. King,* Intel Corporation

To continue the aggressive scaling of integrated circuit feature size demanded by current and future technology nodes, the microelectronics industry has turned to multiple patterning techniques to overcome lithography limitations. These techniques use a series of lithography and etch pattern transfer steps that require a variety of photoresist, hardmask, spacer, etch stop, and other specialized layers. These various pattern transfer materials can be categorized into 'colors,' where each color can be uniquely processed. As multiple patterning designs become increasingly complex, a number of different patterning materials with near-perfect etch selectivity will be needed, for which the current selection of materials will not suffice. Many previous etch studies have investigated the effects of plasma conditions on etch rates for common classes of metal and dielectric materials, but fewer have looked at the dependence of etch rates on material composition within a given class, and fewer still have analyzed the relative etch rates of multiple material classes and compositions under identical treatment conditions. We have surveyed etch rates for a wide range (>300) of samples using two common fluorinated etches traditionally used to pattern silicon-oxide-based (CHF_3) and silicon-nitride-based dielectrics (CF_4/O_2). These samples were drawn from material classes falling within the common Si-C-O-N-H composition space (e.g., SiO_x:H, SiO_xC_y:H, SiN_xC_y:H), as well as classes not traditionally considered for patterning applications including hi-*k* dielectrics (e.g., Al_2O_3, HfO_2) and boron-rich solids (e.g., BN:H, BP:H, BC:H). Surveying such a wide range of materials with varying densities and chemical stoichiometries has allowed us to look at both the effect of composition on etch rates as well as the relative etch rates between classes. From this information, we are able to propose materials that may serve as additional etch colors, drawn from within the classes studied, and by extrapolating the observed trends to different composition spaces.

2:00pm **PS-MoA2 An Investigation into the Mechanism of High Selectivity SiO_x and SiN_x Dielectric Etching**, ***Robert Bruce***, *H. Miyazoe, N.P. Marchack,* IBM Research Division, T.J. Watson Research Center*; J. Lee, J.C. Shearer,* IBM Research, Albany, NY*; JM. Papalia, S.U. Engelmann, E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; J.C. Arnold,* IBM Research, Albany, NY

As the semiconductor industry drives critical dimensions smaller for 7nm technology node and beyond, the challenges to dielectric etch for logic and memory chip manufacturing become ever greater. The established method of high performance dielectric etching is to employ a plasma process using a fluorocarbon (FC) gas that provides material-dependent selective deposition and sidewall passivation as the etch proceeds. Depending on the FC gas chemistry, SiO_{-x} will etch selectively over SiN_{-x} or vice versa. We investigate dielectric etch process parameters that influence dielectric material selectivity (SiO_{-x}/SiN_{-x} or SiN_{-x}/SiO_{-x}) and pattern fidelity, including gas type and wafer temperature. We also study the possibility of improving selectivity by separating the FC deposition and etching steps (i.e. atomic layer etching).

2:20pm **PS-MoA3 The Impact of Highly Selective Dielectric Etches on Etch Stop Layers**, ***Andre Labonte***, GLOBALFOUNDRIES*; A. Carr,* IBM*; J.M. Dechene,* GLOBALFOUNDRIES*; J.C. Shearer,* IBM*; J.M. Lucas, B. Messer, A. Metz,* Tokyo Electron America

As the semiconductor industry drives to sub 50nm gate and interconnect pitches, aspect ratios of contact and via structures are increasing. Subsequently, dielectric and etch stop layers are being thinned to mitigate the increase in aspect ratios. Likewise, the ongoing pursuit of scaling, without proportional changes in overlay, are driving the need for ever more selective Self-Aligned Contact (SAC) dry etch processes. As with any plasma, there is the potential to cause plasma damage to exposed surfaces and stop layers. The plasma damaged materials may in turn be susceptible to significant changes in their properties which may enhance or inhibit future removal of the stop layer. Finally, due to the thinner stop layers being used, this change of material properties in a plasma damaged layer may not be limited to the surface of the layer, but may in fact convert the entire film.

In this paper, we discuss an example where a dielectric system, etched with a SAC process, exhibited an unexpected change in the material properties of the underlying etch stop layer. Process partitioning and materials analysis were used to confirm the unexpected result and develop a theory for observed changes.

2:40pm **PS-MoA4 Plasma Etching of High Aspect Ratio Contacts in SiO_2 using $Ar/C_4F_8/O_2$ Mixtures: A Computational Investigation**, ***Shuo Huang***, *C.M. Huard,* University of Michigan*; S. Shim, S. Lee, I.-C. Song, S. Lu,* Samsung Electronics Co., Ltd.*; M.J. Kushner,* University of Michigan

As feature sizes continue to shrink and aspect ratios continue to increase in semiconductor processing, maintaining critical dimensions (CDs) of the features becomes more challenging. This is particularly the case for dielectric etch of high aspect ratio (AR) contacts (HARC), in which aspect ratios of 50-100 are desired. Our interests in this investigation are two challenges in the reactive ion etching of HARC in SiO_2 using $Ar/C_4F_8/O_2$ mixtures. The first is aspect ratio dependent etching (ARDE) where etch rates generally decrease as AR increases. The second is the origin of non-circular vias from nominally initially circular mask openings.

We report on results from a computational investigation of etching of HARCs in SiO_2 using $Ar/C_4F_8/O_2$ mixtures in a tri-frequency capacitively coupled plasma. Modeling of reactor scale and surface chemistry was performed using the Hybrid Plasma Equipment Model (HPEM). The feature scale modeling was performed using a 3-dimensional implementation of the Monte Carlo Feature Profile Model (MCFPM). The reactor utilizes 3 frequencies, two lower frequencies generally less than 10 MHz and 1 higher frequency of 50-100 MHz. For total powers approaching and exceeding10 kW, radical fluxes to the wafer are dominated by CF_x, O and F

due to there being significant dissociation of feedstock gas. Ion fluxes are dominated by Ar^+ and $C_nF_x^+$.

The general trend of ARDE is observed - etch rates decrease with etch depth within a feature and features simultaneously etched show lower etch rates in smaller features. However, peaks in the instantaneous etch rate may occur when the profile becomes tapered, which funnels hot neutrals to the etch front. Factors contributing to ARDE such as molecular transport of neutral species, shading of ions with non-normal incidence and etch front geometry will be discussed. The origin of non-circular vias is likely due to small asymmetries and imperfections in the mask, which are reinforced during the etch process.

Work was supported by Samsung Electronics Ltd., Department of Energy Office of Fusion Energy Science and the National Science Foundation.

3:00pm **PS-MoA5 BEOL & Interconnect Challenges in Memory Scaling**, ***Mark Kiehlbauch,*** Micron Technology **INVITED**

Interconnect challenges in memory are driven by scaling, novel architectures, and novel memories.

As NAND and DRAM scale, the pitch of the lower levels of metal routing shrink concurrently. With the delay in EUV lithography, 193 immersion together with complex pitch multiplication and multipatterning schemes have been implemented. These have etch challenges with regard to LWR, selectivity, and feature scale CDU.

The implementation of so-called More than Moore in memory is primarily TSV and 3D packaging to deliver multichip memory packages with extremely high bandwidth and also memory plus logic packages. Over the past several years, the integration of these technologies into high performance and cost effective packages has driven a continuous refinement of etch requirements.

Finally, new memory technologies have resulted in aggressive scaling of interconnects with unique profile and CDU requirements.

In each case, the process, hardware, and integration approaches to address these problems will be discussed.

4:00pm **PS-MoA8 Control of Uniformity and Ion Energy Distributions in Tri-frequency Capacitively Coupled Plasmas Accounting for Finite Wavelength Effects**, ***Peng Tian**, S. Huang,* University of Michigan*; S. Shim, S. Lee, I.-C. Song, S. Lu,* Samsung Electronics Co., Ltd.*; M.J. Kushner,* University of Michigan

To provide additional means of control of capacitively coupled plasmas (CCPs) for semiconductor processing, multi-frequency systems are being investigated. Current plasma tools now have up to 3 frequencies. The source is typically a high frequency (50-150 MHz) intended to control ionization. The biases, typically low frequencies of a few to 10 MHz, are used to control ion energy distributions. At sufficiently high frequencies, the applied power takes on electromagnetic properties (as opposed to electrostatic) in which the electric field is wave-guided by the plasma sheath, causing constructive and destructive interference over the wafer. In extreme cases, a center-high electric field is produced along with a non-uniform center-high plasma density. The mixing of frequencies in tri-frequency systems (TF-CCPs) has the potential to mitigate finite wavelength effects while also providing opportunities to control IEDs.

In this work, TF-CCPs were investigated using a 2-dimensional hydrodynamic model with a full-wave FDTD (finite-difference-time-domain) solution of Maxwell's equations. Results will be discussed for plasma uniformity and IEDs for Ar and $Ar/C_4F_8/O_2$ gas mixtures at 10s of mTorr, with frequencies of a few MHz, 10 MHz and up to 150 MHz with collective powers of up to 10-15 kW. We found that at these elevated powers, the ability to separately control ion fluxes and IEDs is at best difficult. For these conditions, the system should be viewed as a collective set of 3-frequencies that have symbiotic contributions, as opposed to separate contributions that can be uniquely controlled.

Work was supported by Samsung Electronics Ltd., Department of Energy Office of Fusion Energy Science and the National Science Foundation.

4:20pm **PS-MoA9 Metal Etch Mechanisms Using NH_x and CN-based Chemistry**, ***Nathan Marchack,*** IBM Research Division, T.J. Watson Research Center*; M. Yamazaki, Q. Yang, N. Joy,* TEL Technology Center, America, LLC*; S.U. Engelmann, E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; A. Ranjan,* TEL Technology Center, America, LLC

While numerous processes for generating volatile metal etch products have been established in the field of plasma processing, there remain certain families of elements, e.g. ferromagnetic transition metals and their alloys, which have yet to display similar etch mechanisms. These and similar elements are finding increasing utility in novel memory technologies and thus their patterning at shrinking length scales poses an interesting problem for future technology nodes.

The existence of gas phase organo-metallic precursors such as $M[(CO)]_x$ (where M = Ni, Fe, Co, etc.) has piqued curiosity in seeking pathways to generate such species using NH_3/CO chemistry in the literature[1], however experimental observation of such byproducts in the gas or plasma phase through techniques such as mass spectrometry has not been reported[2]. Older literature may suggest alternative mechanisms involving the reaction of such metals in the gas phase with linear nitriles[3] and amines[4]. We explore potential reactions of such organic species generated in a variety of high density plasma sources, with a focus on defining how parameters such as source power, type, and gas ratio affect the discharge properties.

The results of this study will then be applied to patterned film stacks of commonly reported metal elements (e.g. Ni, Fe, Co) demonstrating a potential means for etching these materials at tighter pitches (<200nm) for line/space and pillar geometry with reduced sidewall residue and minimal hard mask loss.

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4:40pm **PS-MoA10 The Impact of Gate Overlap on Self-Aligned Contact (SAC) Etching**, ***Jeffrey Shearer,*** IBM Research Division, Albany*; A.P. Labonte,* GLOBALFOUNDRIES*; J.M. Lucas, A. Metz,* Tokyo Electron - TTCA*; J.C. Arnold,* IBM Research Division, Albany

In order to maintain aggressive scaling trends, gate and contact pitches have been reduced to a level requiring robust contact-to-gate self-alignment in order to mitigate gate-to-contact short concerns. Developing novel reactive ion etch (RIE) chemistries to achieve the necessary etch selectivity to the gate cap is one of the more critical challenges in integrated circuit (IC) process development and manufacturing. Further complicating the process space is that selectivity is impacted by the contact-to-gate overlap. This overlap can be intentionally modulated by pitch demands, mask design, and contact critical dimension (CD) or unintentionally modulated by contact-to-gate overlay shifts. Data will show a substantial difference in selectivity between one-sided (borderless) and two-sided ("true SAC") contact-to-gate overlaps. As both situations could exist on-wafer, it is increasingly difficult to develop robust processes that can accommodate a variety of different contact designs at the same time. The data will show how process optimization can minimize some of the challenges in developing a robust process space and will explore the parameter space that can maximize the SAC selectivity process window across multiple overlap regimes. Lastly, it will be shown how overetch impacts the selectivity of the gate cap in terms of the contact-to-gate overlap. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

5:00pm **PS-MoA11 Dynamic Plasma Etching of EUV Photoresist for Contact Profile Control and PR Selectivity Improvement**, ***Hongyun Cottle,*** *I. Saraf, A. Metz, P. Biolsi,* TEL Technology Center, America, LLC

Continued pitch scaling of semiconductor devices to 7nm node and beyond dimensions utilizing conventional 193i based multiple patterning techniques is rapidly driving up cost, complexity, and variability control. EUV patterning can be used to mitigate or delay the challenges of pitch scaling through multiple patterning, but introduces new challenges of its own. EUV lithography introduces new types of resists that are thinner and less etch resistant compared to conventional 193nm resists. Interactions of polymers with plasma etch environments can lead to large changes of the polymer material properties and the three-dimensional nanostructures they pattern. Mask deformation during such etch process can lead to changes in nanoscale topography of device features, often with undesirable consequences, such as increased LER and LWR, tip-to-tip degradation, and line wiggling. Plasma etch faces a significant challenge to optimize its process window to enable high yields with EUV patterning.

This paper presents an unique etch process employing a dynamic etch during softmask open to improve EUV photoresist etch selectivity by

greater than two fold while maintaining critical feature dimensions, such as elliptical contact minor vs major axis CD ratio. By carefully controlling the polymer deposition vs. polymer assisted etching temporal cycle, a very thin layer of conformal polymer can be used to precisely etch and transfer the desired pattern. By utilizing a direct current superposition (DCS) technology, EUV photoresist can be treated to improve not only its etch resistant, but also LER and LWR. After the in-situ photoresist treatment, the dynamic etch process initiates and defines the pattern transfer into softmask, followed by etch steps to anisotropically complete the pattern transfer. Reported is the structural characterization pre and post-etch detailing LER and LWR improvement, and shrink ratio control. In addition, a mechanistic model will be proposed based on optical emission spectroscopy (OES) and thin film compositional analysis.

Thin Film
Room 102B - Session TF+PS+SE-MoA

Plasma-based Deposition Techniques and Film Characterization

Moderators: Jim Fitz-Gerald, University of Virginia, Tansel Karabacak, University of Arkansas at Little Rock

1:40pm **TF+PS+SE-MoA1 Microcrystalline Silicon Thin Film Deposited by Tailored Voltage Waveform Plasmas using an $SiF_4/H_2/Ar$ Chemistry and its Application to Photovoltaics**, ***Junkang Wang,*** LPICM, CNRS, École Polytechnique, Université Paris Saclay, France*; M. Elyaakoubi,* TFSC-Instrument, Palaiseau, France*; E.V. Johnson,* LPICM, CNRS, École Polytechnique, Université Paris Saclay, France

For the growth of hydrogenated microcrystalline silicon (µc-Si:H) thin film by low temperature plasma-enhanced chemical vapor deposition (PECVD), silicon tetrafluoride (SiF_4) has recently attracted interest as a precursor due to the resilient optoelectronic performance of the resulting material and solar cell device. However, many questions remain concerning the critical factors determining the quality of the PECVD-deposited film.

Tailored voltage waveforms (TVWs), non-sinusoidal voltage waveforms used to excite radio-frequency capacitively coupled plasma (RF-CCP) processes, has recently been shown to be effective to separately control the maximum ion bombardment energy (IBE) and the ion flux on each electrode. Due to this unique feature, TVWs have attracted considerable research interest in a very short time. When applied to the growth of µc-Si:H film by PECVD, it can provide an elegant approach for one to gain more insight into the physical principles governing film growth and the optimization of process parameters.

To advance knowledge on this subject, we present studies looking at the deposition of µc-Si:H film from SiF_4 using TVWs, particularly focusing on the material's optoelectronic properties and its resulting PIN solar cell device. We underline recently obtained results concerning critical experimental findings: (1) the significant impact of the maximum IBE to the crystalline grains sizes of the deposited films, (2) the considerable different in films' properties resulting from two types of "sawtooth" waveforms, i.e. "sawtooth-up" and "sawtooth-down", which give similar films deposition rates and the maximum IBE but opposite plasma sheath dynamics during processing. The films generated in these studies have furthermore been characterized using the steady-state photoconductivity and steady-state photocarrier grating techniques, analyzing the coplanar electronic transport properties of the material. The modulated photoconductivity method is also utilized to reveal more specific details about the materials' sub-gap density of states. These studies - along with residual gas analysis studies and Fourier transform infrared absorption results - allow us to optimize the appropriate process parameters of such film and its resulting PIN solar cell device using SiF_4 as the precursor.

2:00pm **TF+PS+SE-MoA2 Boron Carbide-Aromatic Composite Films by PECVD: A Novel Approach to Electron-hole Separation**, *B. Dong, A. Oyelade,* University of North Texas*; E.M. Echeverria,* University of Nebraska-Lincoln*; Y-S. Jun, G.D. Stucky,* University of California at Santa Barbara*; P.A. Dowben,* University of Nebraska-Lincoln*;* ***Jeffry Kelber,*** University of North Texas

Many photovoltaic and photocatalytic systems employ band-bending at surfaces or interfaces to achieve electron-hole separation and functionality. Boron carbide-aromatic composites, formed by plasma-enhanced co-deposition of carboranes and aromatic precursors, present an alternative approach where such separation is achieved by aromatic coordination to the carborane icosahedra. Photoemission, density functional theory calculations, and variable angle spectroscopic ellipsometry demonstrate that for orthocarborane/pyridine and orthocarborane/aniline films, with controlled aromatic/orthocarborane ratios between 1:1 and 10: 1, states near the valence band maximum are aromatic in character, while states near the conduction band minimum include those of either carborane or aromatic character. Thus, excitation across the band gap results in electrons and holes on carboranes and aromatics, respectively. Further such aromatic-carborane interaction dramatically shrinks the indirect band gap from 3 eV (PECVD orthocarborane) to ~ 1.6 eV (PECVD orthocarborane/pyridine) to ~1.0 eV (PECVD orthocarborane/aniline), with little variation in such properties with aromatic/orthocarborane stoichiometry. Recent photoabsorbance measurements show that in orthocarborane/pyridine films, the indirect band gap energy is significantly less than the exciton formation energy of 2.1 eV, allowing facile exciton elimination by phonon scattering of electrons into the conduction band at room temperature. The opposite is true for the PECVD orthocarborane film, where the exciton formation energy (2.4 eV) is less than the indirect band gap, inhibiting exciton elimination by electron-hole separation. The enhanced electron-hole separation, narrowed band gap, and significantly increased carrier lifetimes (350 µsec for PECVD orthocarborane/pyridine vs 35 µsec for PECVD orthocarborane), indicate the potential for greatly enhanced charge generation, as confirmed by zero-bias neutron voltaic studies. Those results--an 850% increase in charge generation per B atom for the PECVD pyridine/orthocarborane film relative to the PECVD orthocarborane film--indicate that the enhanced electron-hole separation and band gap narrowing observed for aromatic/orthocarborane films relative to PECVD orthocarborane, have significant potential for a range of applications, including neutron detection, photovoltaics, and photocatalysis.

Acknowledgements: This work was supported by the Defense Threat Reduction Agency (Grant No. HDTRA1-14-1-0041). The authors would like to thank Shireen Adenwalla for technical assistance and discussion. James Hilfiker is also gratefully acknowledged for stimulating discussions.

2:20pm **TF+PS+SE-MoA3 Impact of Pulsing the rf Power and the Precursor Injection on the Structure and Optical Properties of TiO_2 and TiSiO Thin Films Deposited by PECVD**, ***Agnes Granier,*** *S. Elisabeth, R. Michaud, N. Gautier, M. Richard Plouet,* IMN, University of Nantes CNRS, France*; M. Carette,* IEMN CNRS/Université Lille 1, France*; A. Goullet,* IMN, University of Nantes CNRS, France

TiO_2 thin films are good candidates for the development of passive optical components due to high optical refractive index ($1.8 < n < 2.7$ at 633 nm) combined with high transparency in the visible range. They are compatible with semiconductor technologies and can be synthesized at low temperature by plasma enhanced chemical vapor deposition (PECVD). PECVD is known for its ability to prepare amorphous or partially crystallized films at low temperature and to tune the film composition and optical properties. In the case of TiO_2, columnar polycrystalline anatase films can be prepared by PECVD at substrate temperature less than 150°C. Whereas these TiO2 films are very attractive for photocatalysis, their columnar structure and low optical gap (3.2 eV) appear to be drawbacks for optical applications. Adding a small amount of silicon to TiO_2 allows both obtaining amorphous films and increasing the optical gap, which is highly suitable for optical applications.

In this study, TiO_2 and Ti-Si-O films were deposited in a low pressure rf inductively coupled plasma (ICP) from titanium tetraisopropoxide (TTIP - $Ti(OC_3H_7)_4$) and hexamethyldisiloxane (HMDSO - $SiO_2(CH_3)_6$) vapors mixed with oxygen. The structure and chemical composition of the films were investigated by X-ray diffraction, photoelectron spectroscopy, Fourier transform infrared spectroscopy and Raman spectroscopy. The morphology of the thin films was characterized by scanning and transmission electron microscopies. The optical properties were investigated by UV -Visible spectroscopic ellipsometry and absorption spectroscopy. When deposited at the floating potential, the TiO_2 films deposited in the continuous mode in oxygen rich O_2/TTIP ICP plasmas were previously shown to be columnar and highly crystallized in the anatase form. As silicon is added to titanium, the films become amorphous. Their refractive index decreases and their optical gap increases [1].

Here, we investigate the effects of pulsing both the rf power and the precursor injection on the film structure and optical properties.

On the one hand, in the case of TiO_2 and Ti-O-Si films, the pulse frequency was fixed at 1 kHz and the duty cycle was varied from 100 to 10%. Pulsing the power allows to decrease the deposition temperature (down to about 50°C) while conserving the anatase structure in the case of TiO_2 films, so

that anatase and amorphous high refractive index Ti-Si-O films can be deposited on polymer substrates.

On the other hand, TTIP and HMDSO flow rates have been pulsed, either to get benefit from oxygen plasma treatment following oxide deposition or to deposit TiO_2/SiO_2 stacks.

[1] D. Li et al, Plasma Processes and Polymers, 2016

2:40pm **TF+PS+SE-MoA4 Plasma CVD of Boron-Carbon Thin Films from Organoboron Precursors for Next Generation Neutron Detectors, *Mewlude(Maiwulidan) Imam (Yimamu),*** Linköping University, Sweden*; C. Höglund,* Linköping University and European Spallation Source ERIC, Sweden*; R. Hall-Wilton,* European Spallation Source ERIC, Sweden*; J. Jensen,* Linköping University, Sweden*; S. Schmidt,* Linköping University and European Spallation Source ERIC, Sweden*; I.G. Ivanov, J. Birch, H. Pedersen,* Linköping University, Sweden

A novel design for neutron detectors based on thin films that are rich in the ^{10}B isotope has been suggested for the European Spallation Source (ESS), in order to overcome the very limited availability of ^3He. The detector design uses $^{10}B_4C$ films deposited onto both sides of neutron transparent substrates, e.g., Al blades [1]. The use of aluminum (melting point at 660 °C) limits the deposition temperature for CVD processes and the use of chlorinated precursors due to etching of Al by HCl. Therefore, reactive organoborons are evaluated as precursors for these films using both thermal CVD [2, 3] and plasma CVD.

Plasma CVD of B_xC thin films has been studied by introducing the organoborons trimethylboron $B(CH_3)_3$ (TMB) or triethylboron $B(C_2H_5)_3$ (TEB) into a microwave-induced Ar plasma without using any intentional substrate heating. The effect of plasma power, TMB or TEB to Ar ratio and total pressure on the film composition, morphology, density, chemical structure and internal stress were investigated by means of Tof-ERDA, SEM, XRR, XPS and HRXRD, respectively. Tof-ERDA results showed that the highest B/C ratio of 2 was achieved when using TMB at high plasma power. Densification of the films was accompanied by decreasing the total pressure below 0.4 mbar, resulting in a columnar film with densities of 2.16 ± 0.01 g/cm^3. The H content in the films was high (15±5 at. %) due to the low substrate temperature (~300 °C). XPS revealed that films deposited using TMB mainly contained B-C bonds and small contribution from C-C/CH bonds, that was evidenced by the observed amorphous carbon phases in the films by Raman spectroscopy. The internal compressive stresses in the films were increased with the Ar gas flow causing film delamination, while a low flow of Ar showed good adhesion and stress level is less than 300 MPa. In addition, the plasma composition studied by optical emission spectroscopy (OES) showed that BH, CH, C_2 and H lines were the most intensive lines in the spectrum. Considering the high H content in the films, we propose that BH and CH are the most likely species to contribute to the film formation.

[1] R. Hall-Wilton et al. *IEEE NSS/MIC conference record*, **2012**, 4283

[2] H. Pedersen et al. *Chem. Vap. Deposition***2012**, *18*, 221

[3] M. Imam et al. *J. Mater. Chem. C***2015**, *3*, 10898

3:00pm **TF+PS+SE-MoA5 Plasma Enhanced Atomic Layer Deposition of Superconducting Nb_xTi_yN Films, *Mark Sowa,*** Ultratech/CNT*; Y. Yemane, J. Provine,* Stanford University*; E.W. Deguns,* Ultratech/CNT*; F. Prinz,* Stanford University

NbN, TiN, and their mixtures have been studied for their use in superconducting applications. These materials are commonly deposited via sputtering techniques, but a lack of thickness control limits this technique from applying thin, uniform films. Atomic Layer Deposition (ALD) has been widely recognized for its ability to coat substrates with uniform film thicknesses ranging from a few Ångstroms to 100's of nanometers. Plasma Enhanced ALD (PEALD) extends the capabilities of the ALD technique, improving the properties of certain films, particularly nitrides deposited at low temperatures. PEALD of NbTiN has previously demonstrated superconducting properties[1] and PEALD NbN has been previously reported with a critical temperature of 10.4K [2].

In this work, Nb_xTi_yN ($0 \le x, y \le 1$) has been deposited using PEALD in an Ultratech/CNT Fiji system at substrate temperatures between 100 and 300°C. Stoichiometry was controlled by adjusting the ratio of NbN:TiN cycles during the film deposition. Precursors utilized for this study were (t-butylimido) tris(diethylamido) niobium (TBTDEN) and tetrakis(dimethylamido) titanium (TDMAT). A mixture of N_2 and H_2 was used as the plasma gas for the NbN cycles while TiN was deposited with an N_2 plasma. Films were analyzed for thickness and optical properties through spectroscopic ellipsometry. Room temperature resistivity was derived from four point probe measurements. Samples were analyzed with X-ray photoelectron spectroscopy to determine stoichiometry and impurity levels. Superconductivity characteristics of the films will also be presented.

A 20nm, 300°C deposition of NbN, which had a room temperature resistivity of 282μΩ-cm, was shown to have a critical temperature of 12.4K and a critical field greater than 12 Tesla.

[1] E. F. C. Driessen, et al., "Strongly Disordered TiN and NbTiN s-Wave Superconductors Probed by Microwave Electrodynamics," Phys. Rev. Lett. 109, 107003, 2012.

[2] M. Ziegler, et al., "Superconducting niobium nitride thin films deposited by metal organic plasma-enhanced atomic layer deposition," Supercond. Sci. Technol. 26 (2013) 025008.

3:20pm **TF+PS+SE-MoA6 Mechanical Reliability of PECVD Barrier Films for Flexible Electronics, *Kyungjin Kim,*** *A. Singh, H. Luo, T. Zhu, O. Pierron, S. Graham,* Georgia Institute of Technology

The development of PECVD and ALD barrier films have proven to be viable approaches to create barrier films for flexible electronic applications. While much research has focused on the water vapor transport properties of these films, the mechanical reliability during flexural deformation is critical to the performance and durability of these coatings. Overall, the use of the critical onset strain is limiting in trying to define the limits of performance since it ignores time-dependent processes that can occur during mechanical deformation. In this work, we investigate the time-dependent channel crack growth behavior of silicon nitride and ALD barrier films on polyethylene substrates in humid and dry air. The evaluation of the cracking process versus applied strain and load was measuring in-situ using optical and laser scanning confocal microscopy. The results show that crack growth can occur at strains that are much lower than the standard measured onset critical strains. The results of the work show that both polymer relaxation of the PET substrate as well as environmentally assisted crack growth occurs in the films, both in a time dependent manner. Tests in dry air versus tests in humid air show crack growth rates increasing from 100 nm/s to 10 um/s for an applied stress intensity factor of 1.6 MPa.m^0.5. In addition to the dramatic changes in crack growth rates with environmental conditions, larger crack densities were observed in humid environments. This suggests an easier initiation and growth of crack in humidity versus dry air. Overall, the results presented will show the strong link between environment, temperature, and the rate at which cracks grow in barrier films. Finally, the energetics of the crack growth process will be presented as a better metric than onset crack strain to evaluate the mechanical reliability of the barriers for a given application.

4:00pm **TF+PS+SE-MoA8 Origin of Stress in Sputtered CdTe and ZnS Films: Influence of Sputter Ion Mass on Mechanical and Chemical Layer Properties, *Ségolène Liénard,*** Univ. Grenoble Alpes, LTM CNRS, 38000 Grenoble, France*; D. Sam-Giao, A. Kerlain,* Sofradir, BP 21-38113, Veurey-Voroize, France*; F. Boulard, C. Vallée,* Univ. Grenoble Alpes, France

Physical vapor depostion is a mature, well understood and established technology in integrated circuit fabrication. CdTe and ZnS binary II-VI compounds materials are commonly used in photovoltaic solar cells or infrared optics. However, sputtering deposition of these materials still suffer from a lack of comprehensive study to optimize process integration.

Our study is focused on the influence of projectile ions mass on properties of sputtered deposition CdTe and ZnS films. We compare physico-chemical, mechanical and electrical properties of CdTe and ZnS films deposited with Ar and Xe ions as sputter gas. Ar and Xe concentration in these films are characterized by Time of Flight Secondary Ions Mass Spectrometry (TOF-SIMS). Dedicated implanted reference samples are used to quantify the absolute concentration. Layers microstructures are characterized by Scanning Tunneling Electron Microscopy (STEM) and dielectric constant by capacitance-voltage measurements. We use the curvature method based on the well known Stoney concept [1] to calculate film stress while density is estimated by differential weighing.

With Ar ion deposition process (low sputter on target mass ratio), we observe Ar and cavities inside the CdTe layer. The density as well as the dielectric constant are below bulk values. A good agreement is found between the cavity density and the effective dielectric constant

determined by the Bruggeman model [2-3]. on the contrary, Xe ion target sputtering (high sputter on target mass ratio) leads to denser films, without Xe inside the layers, and close to theory density and dielectric constant values. We discuss these observations in terms of backscattered ions incorporation. Moreover, the effect of thermal annealing time on stress evolution is discussed in regards of Ar or Xe incorporation and outgasing.

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[2] Aspnes D. E., Thin Solid Films 89 (1982) 249.

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4:20pm **TF+PS+SE-MoA9 Synthesis and Characterisation of MoB_{2-x} and Mo-B-C Thin Films by Non-Reactive DC Magnetron Sputtering**, ***Paulius Malinovskis,*** Uppsala University, Sweden*; J.P. Palisaitis,* Linkoping University, Sweden*; P.O.A. Persson,* Linköping University, Sweden*; E.L. Lewin, U.J. Jansson,* Uppsala University, Sweden

Transition metal diborides (MeB_2) with the AlB_2-type structure have many unique properties such as high hardness, high conductivity and oxidation resistance One of the most studied diboride compounds is TiB_2 but also other transition metals like Cr, Nb and Mo can form the simple AlB_2 type structure.

Non-reactive magnetron sputtering is an excellent technique to deposit thin films of different MeB_2 phases. It is well-known that phases with rather simple crystal structures are preferably formed in magnetron sputtering where the quenching rates of the incoming atoms are high. Such metastable MeB_2 films may be chemically more reactive in a tribocontact and form a lubricating tribofilm of metal oxides and layered BO_x. Some metal oxides such as MoO_3 and boric acid (forming in humid atmosphere from BO_x) have been predicted to exhibit low friction coefficients. Consequently, it is possible that metastable MeB_2 films with the AlB_2-structure may exhibit excellent low friction properties. Another way to tailor metal diboride properties is to alloy it with third element, e.g. carbon.

In this study we have investigated the microstructure, mechanical and tribological properties of DC magnetron sputtered MoB_{2-x} and Mo-B-C thin films from Mo/B and graphite carbon target. The films were characterized with XRD, XPS, TEM, nanoindentation and tribological ball-on-disk method. All films exhibited the AlB_2-type structure with substoichiometric MeB_{2-x} grains surrounded by a tissue phase of a-B and a-BC_x. The MoB_{2-x} films were substoichiometric with respect to boron and exhibited a much higher hardness compared to bulk samples, which could be attributed to a hardening effect of the tissue phase. Friction measurements confirmed the hypothesis that a significant tribofilm formation is present on the metastable MoB_{2-x} films. However, a reduced friction coefficient could not be observed. Addition of carbon resulted in a change in the composition of the tissue phase. This caused a reduction in hardness and a reduction of the friction coefficient. General trends in the phase formation and properties of Mo-B-C films will be explained in detail and compared with other Me-B-C systems (Me= Ti, Cr, Nb).

4:40pm **TF+PS+SE-MoA10 Molybdenum Back Contacts Deposited by High Power Impulse Magnetron Sputtering**, *D.A. Loch,* ***Arutiun Ehiasarian,*** Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the $Cu(InGa)Se_2$ absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^{0} Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick films. The correlation between resistivity, microstructure, crystallographic texture, stress and deposition flux characteristics is discussed.

5:00pm **TF+PS+SE-MoA11 Plasma Characterization of Al and Cu with HIPIMS**, ***Jason Hrebik,*** Kurt J. Lesker Company*; R. Bandorf, H. Gerdes, D. Spreemann,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

High power impulse magnetron sputtering (HIPIMS) is a well-known technique for tailoring the coating properties in comparison to DC. In many cases the thin films were developed in smaller scale R&D facilities and afterwards transferred to industrial scaled machines. But the source configuration, magnetic field, and overall mechanical layout differs for the larger sputtering plant, and therefore a direct upscaling of the process is quite difficult. Since often the thin film properties are correlating with the plasma properties, plasma characterization is very useful tool for determining the main important parameters for a process transfer.

This investigation is focused on the plasma characterization of Al and Cu on a small circular target (3 inch) and will give a short comparison to a rectangular target (10 inch by 15 inch). As plasma properties the ion density and the optical emission was measured. The measurements were carried out in a time resoled mode and can be correlated to target voltage and current.

Plasma Processing for Biomedical Applications Focus Topic
Room 101A - Session PB+BI+PS-TuM

Plasma Processing of Biological/Biomimetic Surfaces

Moderators: Uroš Cvelbar, Jozef Stefan Institute, Slovenia, Satoshi Hamaguchi, Osaka University, Japan

8:00am **PB+BI+PS-TuM1 Investigation of Discharge Propagation on Cell and Plasmid Suspension in Plasma Gene Transfection**, ***Yugo Kido***, Pearl Kogyo Co., Ltd., Japan; *H. Motomura, Y. Ikeda,* Ehime University, Japan; *S. Satoh,* Y's Corp., Japan; *M. Jinno,* Ehime University, Japan

The authors have been developing a plasma gene transfection technique and averaged transfection efficiency up to 20% and cell survivability up to 90% are achieved for more than 20 kinds of cells. A typical procedure of this method is as follows. Target cells are cultured on a 96 well plate and gene suspension is added. The plate is placed between a high voltage electrode made of copper capillary with the diameter of 70 µm and a copper plate grounded electrode. By exposing the suspension to a microplasma generated at the tip of the capillary electrode, the cells are transfected by the genes. In this method, both chemically reactive species (chemical factors) and discharge current (electrical factors) are indispensable to the transfection process and their synergistic effect has been experimentally verified. Moreover, the transfection occurs on the whole area of each well although only the central area is exposed to the microplasma. In this study, to clarify how the discharge current contributes the transfection process with the synergistic effect with the chemical factor, discharge propagation phenomenon on the cell and plasmid suspension is investigated.

As a target, COS-7 cells are cultured on a 35 mm dish and 24 µg of plasmid pCX-EGFP suspended in 120 µL of TE/PBS buffer is added. The applied voltage between the electrodes is 20 kHz sinusoidal waveform and the amplitude is set at 10 kV peak to peak. The gap length between the capillary electrode and the suspension is set at 1 to 5 mm. The discharge propagation is observed with an ICCD camera equipped with a UV lens.

When only TE/PBS buffer solution exists in the dish, the discharges reach the buffer solution surface and then they propagate radially up to 15-20 mm of diameter. On the other hand, when the cells are cultured on the dish, remarkable radial propagation of the discharge is not observed and the discharge irradiation area is limited within the diameter of about 1 mm, which is narrow compared with the area in which the transfection occurs. Therefore, as a contribution of the electrical factors, not only the direct effect of the discharge current, charge on the plasmids, conduction current in the solution etc. should be analyzed. As a first step of the chemical factor investigation, similar observation is performed by the ICCD camera with an interference filter to observe the emission of OH radicals. The results of the discharge propagation paths study by means of equivalent circuit simulation and comparative analysis between the discharge propagation and the transfection will be shown at the symposium.

8:20am **PB+BI+PS-TuM2 Spectroscopic Study of Permeability of Stratum Corneum by Plasma Treatment for Transdermal Drug Delivery**, ***Jaroslav Kristof***, *N. Tran, M. Blajan, K. Shimizu,* Shizuoka University, Japan

Application of drugs by needles presents risk of infections and causes pain. On the other side, oral application of drugs can be toxic for human body because drug has to be transported through alimentary tract and higher amount of active agent is required. Transdermal delivery could be ideal painless and effective way but barrier function of skin has to be reduced for improving permeability of drugs. Research of last years proves that plasma can interact with skin and cause decreasing barrier function of skin [1-3].

We used plasma jet and microplasma discharge for investigation of barrier function of stratum corneum – horny layer of of Yucatan micropig skin. Helium or argon was used as working gas. These rare gases were later enriched by liquids like water or ethanol through the bubbling system to achieve higher amount of active particles like OH.

Physical changes of the pig skin were observed by microscope. As the human body is not non-conductive, we can expect different results when conductivity of layer under skin is changed. We compared effect of plasma on conductive and non-conductive material. Placement of skin on conductive material caused burned spots on skin by plasma jet [3]. While it was isolated, no damage was observed with plasma jet irradiation. In case of treatment of skin by microplasma, physical damage was hardly observed.

Changes in stratum corneum layer were observed by Attenuated Total Reflectance – Fourier Transform InfraRed (ATR-FTIR) spectroscopy. ATR-FTIR spectrum offer information about water, lipid bilayer and proteins in stratum corneum. Permeability of skin for drugs correlates with shift of asymmetric stretch of CH_2 band to higher wavenumbers. This information describes behavior of lipid bilayer. Information about reaction of proteins on plasma treatment content Amide I and Amide II bands. Reaction of stratum corneum layer of pig skin depended on used discharge type and gas. Effectivity of plasma sources and used gases or gas mixtures for transdermal drug delivery was analysed.

References

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8:40am **PB+BI+PS-TuM3 Cell Attachment to Microwave Plasma-oxidized Titanium and Titanium Alloy Substrates**, ***Denis Dowling***, University College Dublin, Ireland; *M. Naciri,* University Mohamed V of Rabat, Morocco; *M. Al-Rubeai, A. Breen,* University College Dublin, Ireland **INVITED**

Titanium and its alloys have been widely investigated for use in orthopedic and dental implant devices, particularly for osteointegration and bio-compatibility. This paper evaluates the influence of titanium surface oxidation using a microwave plasma treatment technique on cell attachment. Commercially pure titanium (CpTi) and titanium alloy (Ti6Al4V) discs were treated in an oxygen atmosphere for 5 min-utes at 850 °C using a microwave (2.45 GHz) plasma system, operating at 2 kPa. After the 5-minute treatment, the thickness of the oxidized layer was 2.3 µm on the CpTi discs and 4.7 µm on the Ti6Al4V discs, with growth rates of 0.5 and 1 $\mu m.min^{-1}$ respectively. Reduced plasma oxidation rates were observed on a high surface area beaded surface (Porocoat). In contrast to the plasma treatments, the use of air furnace oxidation only achieved an oxide layer thickness for the CpTi of 1 µm, when treated at the same temperature. Optical profilometry measurements were performed to determine the surface roughness; XRD, EDX, and SEM examinations were also car-ried out to determine the properties of the oxide layers and their morphologies. Cell attachment to the treated discs was also assessed after exposure times of 25 and 100 minutes. A 40% increase in MG63 osteoblast cell attachment on the Ti6Al4V discs was observed, when compared with that on the CpTi discs. Alkaline phosphatase (ALP) specific activity of MG63 cells grown on control and plasma oxidised surfaces were compared after 21 days. A statistically significant difference between Ti6Al4V and CpTi oxidised surfaces ($P<0.05$), when compared to that obtained for the control surface that had not been plasma treated. The acicular morphology of the oxidised Ti6Al4V surface was found to have the most significant influence on enhancing cell attachment, combined with higher oxide layer roughness and thickness.

9:20am **PB+BI+PS-TuM5 The Role of Electrical and Chemical Factors in the Molecular/Gene Transfection by Micro-Plasma Irradiation**, ***Masafumi Jinno***, *Y. Ikeda, H. Motomura,* Ehime University, Japan; *Y. Kido,* Pearl Kogyo Co. Ltd., Japan; *S. Satoh,* Y's Crop., Japan **INVITED**

The plasma gene transfection is expected as a safe and useful method of gene transfection. However, this method had a problem of a difficulty in keeping both high transfection efficiency and less cell damage simultaneously. The authors have evaluated four different plasma sources, such as arc discharge, plasma jet, DBD (dielectric barrier discharge) and microplasma, in terms of the transfection efficiency and the cell viability. High transfection efficiency is achieved by the styles of arc discharge and microplasma in which the electric current flows via the cells. Our experimental results suggests that an electric current may play an important role in plasma gene transfection, and that total volume of the gas flow must be small or zero and the area in which the cells are directly irradiated by plasma must be small in order to achieve higher cell viability. Among the various types of plasmas, which the authors have tried, the microplasma satisfies these conditions and brings both the high transfection efficiency and the high cell viability simultaneously.

We evaluated the contribution weight of three groups of the effects and processes inducing gene transfection, i.e. electrical, chemical and biochemical ones through three experiments. The laser produced plasma (LPP) was employed to estimate the contribution of the chemical factors. The liposomes were fabricated and employed to evaluate the effects of plasma irradiation on membrane under the condition without biochemical

reaction. The clathrin-dependent endocytosis, one of the biochemical processes was suppressed. It also turned out the clathrin-dependent endocytosis is the process of the transfection against the 60% in all the transfected cells. The endocytosis and electrical poration are dominant in plasma gene transfection, and neither permeation through ion channels nor chemical poration is dominant processes.

By scavenging the H_2O_2 generated by plasma irradiation using catalase, the transfection efficiency decreased to 40% of that of without catalase. On the other hand, when the H_2O_2 solution is dropped in the cell suspension without plasma irradiation, the transfection is not observed. These results suggest that the synergistic effect of H_2O_2 with electrical factors or with other reactive species generated by plasma irradiation is important. Consequently it becomes clear that chemical factors, radicals such as H_2O_2 and reactive oxygen/nitrogen species, do not work by itself alone, and that the electrical factors (electrical current, charge and field) are essential to plasma gene transfection.

11:00am **PB+BI+PS-TuM10 Control of Plant Growth by RONS Produced Using Nonthermal Atmospheric Air Plasma**, ***Kazunori Koga,*** Kyushu University, Japan*; T. Sarinont,* Kyushu University*; M. Shiratani,* Kyushu University, Japan

Nonthermal atmospheric plasmas have been widely used for biomedical applications because of their non-equilibrium feature and synergy effects [1-3]. The non-equilibrium feature allows us to introduce reactive oxygen and nitrogen species (RONS) to biomaterials with a significantly wide dose range compared with the conventional irradiation methods such as X-ray and γ-ray [4]. For an agricultural application, we succeeded in reducing harvest period and enhancing crop yield by plasma irradiation to plant seeds [5]. We found irradiation of RONS with an appropriate dose to seeds brings about growth enhancement in all growth stages of plants. To understand the growth enhancement mechanism, here we have studied dependence of irradiation dose of RONS produced by plasma to seeds on growth of *Arabidopsis thaliana L.* Experiments were carried out using a scalable DBD device [2, 3, 5]. The device consisted of 20 electrodes of a stainless rod of 1 mm in outer diameter and 60 mm in length covered with a ceramic tube of 2 mm in outer diameter. The discharge voltage and current were 9.2 kV and 0.2 A. 20 seeds of Arabidopsis thaliana L. were set 3 mm below the electrodes. The RONS dose was controlled by the irradiation time. After plasma irradiation, they were grown on soil tab in incubators. To evaluate plant growth, the stem length was measured as a function of cultivation days. The stem length was normalized by the stem length of the plants without plasma irradiation. To evaluate statics of the measured values, we used a two-tailed ANOVA statistically significance different at $\alpha = 0.05$ ($p < 0.05$). The normalized stem length increases to 1.3 for 3 min irradiation, then decreases to zero for 10 min irradiation. The results indicate the plant growth is activated by plasma irradiation less than 3 min and inactivated by plasma irradiation of 5-10 min. Above 10 min irradiation, no seeds were germinated. We have succeeded in growth control of plants from death to activation with irradiation dose of RONS produced by plasma. The mechanism will be discussed in the presentation.

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11:20am **PB+BI+PS-TuM11 Generation of Reactive Species in Medium Irradiated Laser-Induced-Plasmas**, ***Yukihiro Kurokawa,*** *N. Kurake, K. Takeda, K. Ishikawa, H. Hashizume, H. Tanaka, H. Kondo, M. Sekine, M. Hori,* Nagoya University, Japan

The non-equilibrium atmospheric pressure plasma (NEAPP) was irradiated to the cell culture medium as liquid. The antitumor effect, showing the selective killing effect for cancer cells without killing normal human cells, was reported [1,2]. This effect are considered to be caused by large amounts of reactive nitrogen and oxygen species (RONS) generated by the plasma. However, chemical reactions during transport of plasma in ambient to the liquid surface is complicated; therefore we have applied the laser-induced plasma.

Previously, we reported that the high ratio of NO_2^-/ H_2O_2, even in low H_2O_2 contained in the plasma activated medium [3]. However, relations of reactive species concentrations with antitumor effects have not been fully elucidated. Here, we focus on the concentrations of reactive species generated in culture media by the laser-induced plasma.

A Nd:YAG laser and harmonic generators (Quanta Ray Pro 230, Spectra Physics) provided the pulsed-laser light with a wavelength of 266 nm, a frequency of 30 Hz, a power at sample surface of 25 mW. The light was focused on the gas-liquid interface of ultrapure water or Dulbecco's Modified eagle Medium (DMEM; cat. no. 5796; Sigma) by using plano-convex lens, made of synthetic quartz. 2 mL of the liquid was typically irradiated for 5 min. This is called as LPAM. Just after irradiation, H_2O_2 and NO_2^- concentrations were measured by using absorption that was measured by ultraviolet-visible near infrared spectrometer (V-650, JASCO). Moreover, HeLa cells were incubated in the LPAM and cell survival was measured after 24 h incubation. For analysis of killing mechanism, activated caspase3/7 as apoptosis marker (CellEvent Caspase-3/7) was measured after fluorescent staining by a fluorescent microscope.

The LPAM generated effectively H_2O_2 causing by photo-dissociation of water, hydroxyl radicals (・OH) works a precursor of H_2O_2 with the reaction of ・OH + ・OH →H_2O_2. Survival of HeLa cells in the LPAM was dependent on dilution of the LPAM and standard DMEM. We prepared the diluted LPAM for a half of killing of HeLa cells. After the cultivation for 24 h in the diluted LPAM, the caspase-3/7 activity of dead cells as apoptosis death was observed clearly. Notably, the cell-death was almost inhibited by catalase.

We will discuss on the generation mechanism of active species and the mechanism of antitumor effect of the LPAM with comparison of the PAM.

This work was partly supported by MEXT KAKENHI on Innovative Areas Grant no. 24108002.

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11:40am **PB+BI+PS-TuM12 Electric Fields in kHz-driven Plasma Jets**, *ET. Slikboer, Y.N. Nguyen,* Eindhoven University of Technology, The Netherlands*; O.Y.N. Guaitella,* Ecole Polytechnique, Palaiseau, France*; G. Sretenović,* University of Belgrade*; A. Obrusnik,* Masaryk University, Brno*;* ***Ana Sobota,*** Eindhoven University of Technology, The Netherlands **INVITED**

Non-thermal atmospheric pressure plasma jets have been developed for use on thermosensitive targets at atmospheric pressure, for example polymers or for biomedical applications. Diagnostics on these plasma sources is challenging because of their transient nature, often associated jitter and very small volume. Electric fields, fundamental property essential for the understanding of the discharge, are not well known. In this talk two methods of electric field measurements will be shown applied to a He kHz-driven jet, one based on spectroscopy and one on polarimetry and the obtained results will be discussed.

Plasma Science and Technology
Room 104B - Session PS-TuM

Plasma Diagnostics, Sensors and Control

Moderator: Michael Gordon, University of California at Santa Barbara

8:00am **PS-TuM1 Translational and Vibrational Energy in Cl_2 and O_2 Plasmas Probed by Innovative Optical Diagnostics**, ***Jean-Paul Booth,*** *D. Marinov, M. Foucher, O.Y.N. Guaitella,* LPP-CNRS, Ecole Polytechnique, France*; C. Drag,* Laboratoire Aime Cotton, CNRS-U. Paris-Sud, France*; A. Agarwal, S. Rauf,* Applied Materials Inc. **INVITED**

A common assumption for "Low-temperature" plasmas is that neutral molecules and atoms in the system are in thermal equilibrium with the surrounding ambient (room) temperature, and only charged particles, which can acquire energy from applied electric fields, have higher mean energies. In reality, energy can be transferred from electrons or ions to the neutral gas, increasing the gas translational temperature. Furthermore, non-equilibrium vibrational or rotational distributions can occur in molecular gas plasmas. This can have significant effects on the plasma dynamics. Firstly, since most plasma reactors operate in a pressure-controlled regime, high gas temperatures will cause a considerable decrease in gas density (and therefore in electron-neutral collision rates). Secondly, the rates of activated processes may be significantly increased by translational energy. Vibrational excitation can lead to large increases in the rates of electron dissociative attachment and neutral dissociation. We have developed a new, unambiguous technique to measure gas translational temperature of atoms, using Doppler-resolution Two-Photon Absorption Laser Induced Fluorescence (HR-TALIF) employing a specially-built narrow-bandwidth tuneable pulsed UV laser. Initial results have been obtained on oxygen atoms, where a measurement precision of ±10K is

readily obtained. In a DC glow discharge in pure O_2 the gas temperature up to 550K are observed. The technique will be extended to the study of lower-pressure inductively-coupled plasmas, where higher temperatures are expected, and to chlorine atoms.

In order to investigate vibrational distributions, we have developed a high-sensitivity ultra-broadband ultraviolet absorption spectrometer. This employs a highly-stable laser-plasma light source and achromatic optics, allowing absorption spectra over a 250nm range to be measured with a baseline stability of the order 10^{-5}. In pure O_2 discharges (both DC glow and in a low-pressure ICP reactor) we were able to observe oxygen molecules in vibrationally-excited levels up to v=18 (more than half-way to dissociation), with a "tail" vibrational temperature of 7000K. Vibrational excitation was also detected in Cl_2 molecules in a pure Cl_2 ICP. However, Cl_2 appears to be close to thermal equilibrium with the gas translational temperature, which nevertheless approaches 2000K in this case.

This work was performed within the LABEX Plas@par project, and received financial state aid managed by the Agence Nationale de la Recherche, as part of the programme "Investissements d'avenir" under the reference ANR-11-IDEX-0004-02 and ANR project CleanGRAPH ((ANR-13-BS09-0019).It was also supported by the Applied Materials University Research Partnership Program

8:40am **PS-TuM3 Spectroscopic Measurement of Molecular Densities and Temperatures in Processing Plasmas**, ***Yaser Helal***[*], *C.F. Neese, F.C. De Lucia,* The Ohio State University*; A. Agarwal, B. Craver, P.R. Ewing, P.J. Stout, M.D. Armacost,* Applied Materials, Inc.

Processing plasmas are of a similar pressure and temperature to the environment used to study astrophysical species in the submillimeter/terahertz spectral region. Many of the molecular neutrals, radicals, and ions present in processing plasmas have been studied in the laboratory and their absorption spectra have been cataloged or are in the literature for the purpose of astrophysical study. Thus, the methods developed over several decades in the submillimeter spectral region for these laboratory studies are directly applicable for use in the semiconductor manufacturing industry. In this work, a continuous wave submillimeter absorption spectrometer was developed to study its viability as a remote sensor of gas and plasma species. A major advantage of intensity calibrated rotational absorption spectroscopy is that it can be used to determine absolute concentrations and temperatures of plasmas species from first principles without altering the plasma environment. An important part of this work was the design of the optical components which manage the coupling of the 500 – 750 GHz radiation through a commercial inductively coupled plasma (ICP) etch chamber using its existing viewport. A software routine was developed to simultaneously fit for background and absorption signal. The absorption signal determines the concentration, rotational temperature, and translational temperature of polar species. Examples of measurements made in ICPs will be demonstrated.

9:20am **PS-TuM5 Pulsed Capacitively Coupled Plasma Ignition: PROES and RF-IV Diagnostics**, ***John Poulose***, *M.J. Goeckner, L.J. Overzet,* The University of Texas at Dallas

Pulsed plasma ignition induces rapid changes to the electron energy distribution function. These transitions are of particular interest in the application of etching and deposition of semiconductors. In this article we report temporally and

spatially resolved measurements of the optical emission intensity and RF current and voltage for 1 kHz pulsed plasmas in both electropositive (Ar) and electronegative (CF4=O2=Ar) gas mixtures. This allows us to develop a better understanding of the transients during the beginning and end of the powered component of the RF pulse. We are able show the development of the plasma sheath early in the pulse by combining phase resolved optical emission intensity measurements with measurements of the radio frequency power delivery. In the electronegative discharge we find that the sheath width is minuscule early in the pulse but then expands rapidly. The rapid expansion results in a wave like phenomenon with negative ions bouncing between the growing sheaths.

9:40am **PS-TuM6 Control of Ion Energy Distributions on Insulating Surfaces using Pulsed Plasmas**, ***Tyler List***, *T. Mu, V.M. Donnelly, D.J. Economou,* University of Houston

As the requirements for plasma etching become more stringent, the need for plasmas that can produce monoenergetic ion energy distributions (IED) keeps increasing. The problem of charging inside of insulating features also becomes magnified at smaller feature sizes, which result in higher aspect ratios. A process in which electrons can reach and neutralize charged features is important to creating nearly monoenergetic IEDs. An argon RF pulsed plasma with synchronous DC boundary voltage was used to generate a nearly monoenergetic IED. To minimize charging of insulating surfaces, short positive voltage pulses were applied to the chuck holding the substrate during the afterglow, capacitively-coupling to the substrate surface and causing electrons to reach the surface and neutralize the surface charge. This allows a self-limited, nearly grounded surface potential to be achieved. Consequently, positive ions can reach the surface without slowing down by positive surface charge. The ion energy therefore is equal to and controlled by the plasma potential relative to ground, set by a synchronous bias voltage in the afterglow of the pulsed plasma. Surface potential measurements confirmed that DC chuck pulses temporarily neutralize the surface charge. Retarding field energy analyzer measurements performed on the floating chuck with the pulsed plasma and no boundary bias or chuck bias pulses showed an IED with a large very low energy peak (~0-2 eV) and a low energy peak (~10 eV, depending on pressure), corresponding to the power off and power on portions of the cycle, respectively. When the boundary bias and chuck pulses are applied in the afterglow, these peaks change slightly and a third peak appears at an energy near that of the boundary bias voltage. Analysis of the passive charging rate on the surface allowed the prediction of optimal pulsing frequency. Careful tuning of the other chuck pulsing width and amplitude, as well as the pulsed plasma parameters, also improves control of the IED.

11:00am **PS-TuM10 Charged Particle Dynamics in Technological Radio Frequency Plasmas Operated in CF_4**, ***Julian Schulze***, West Virginia University*; B. Berger,* Ruhr-University Bochum, Germany*; S. Brandt,* West Virginia University*; B. Bruneau,* Ecole Polytechnique, Palaiseau, France*; Y. Liu,* Dalian University of Technology*; I. Korolov, A. Derzsi,* Hungarian Academy of Sciences*; E. Schuengel, M. Koepke,* West Virginia University*; T. Mussenbrock,* Ruhr-University Bochum, Germany*; E.V. Johnson, T. Lafleur, J.-P. Booth,* Ecole Polytechnique, Palaiseau, France*; D. O'Connell, T. Gans,* University of York, UK*; YN. Wang,* Dalian University of Technology*; Z. Donko,* Hungarian Academy of Sciences **INVITED**

The spatio-temporal dynamics of charged particles and the formation of ion energy distribution functions (IEDF) are investigated in electronegative capacitive RF plasmas operated in CF_4 based on a combination of experiments, PIC simulations, and models. In the experiment, Phase Resolved Optical Emission Spectroscopy is used to access the space and time resolved electron dynamics. The DC self bias and IEDFs are measured at the electrodes. For a single frequency discharge operated at 13.56 MHz and 80 Pa we demonstrate that the presence of an electronegative gas can change the electron power absorption dynamics completely compared to electropositive gases by inducing a heating mode transition. Reducing the driving frequency results in the formation of stable striations of the optical emission and electron impact excitation rate due to the collective response of positive and negative ions to the driving frequency. Based on this fundamental understanding, we show that tailoring the driving voltage waveform using a superposition of multiple consecutive harmonics of a fundamental frequency with individually adjustable harmonics' amplitudes and phases allows for control of the DC self bias, the shape and mean energy of the IEDF, the electron power absorption dynamics, and the spatial division of the discharge into two halves of strongly different electronegativity.

11:40am **PS-TuM12 Correlation of III/V Semiconductor Etch Results with Physical Parameters of High Density Reactive Plasmas Excited by Electron Cyclotron Resonance**, ***Gerhard Franz***, Munich University of Applied Sciences, Germany*; R. Meyer, M.-C. Amann,* Technische Universität München, Germany

Reactive ion etching is the interaction of reactive plasmas with surfaces. For a

detailed understanding, significant properties of reactive composite low pressure

plasmas driven by electron cyclotron resonance were investigated and compared with

the radial uniformity of the etch rate. The determination of electronic properties

of chlorine and hydrogen containing plasmas enabled the understanding of the

pressure dependent resonance behavior and gave a better insight into the

[*] **Coburn & Winters Student Award Finalist**

electronic parameters of reactive etch gases. With electrical evaluation of I(V) characteristics obtained with a Langmuir probe, differently composed plasmas were investigated and the most important methods of analyzing the I(V) characteristics were compared. A mathematical model to reduce noise sensitivity was used and compared to the standard method of Druyvesteyn to derive the electron energy distribution functions. Special attention was payed to the power of the energy dependence in the exponent. Especially for plasmas which are generated by electron cyclotron resonance with EM modes, the existence of Maxwellian distribution functions are not to be taken as a self-evident fact, but it was proven for Ar- and Kr-stabilized plasmas. Aside from the electron temperature, which could be derived within a certainty of ten percent using the discussed methods, the global uniform discharge model of Lieberman has been shown to be useful to calculate the neutral gas temperature. To what extent the invasive method of using a Langmuir probe could be replaced with the non-invasive optical method of emission spectroscopy, especially actinometry, was investigated and the resulting data showed the same relative behavior as Langmuir data.

12:00pm **PS-TuM13 Mapping Plasma Potential of Rotating Ionization Zone in DC Magnetron Sputtering**, ***Matjaz Panjan***, Lawrence Berkeley National Laboratory, Slovenia; *A. Anders,* Lawrence Berkeley National Laboratory

In the magnetron discharges formation of dense plasma structures, called ionization zones or spokes, have been extensively studied over the last few years. Ionization zones were first observed in high power impulse magnetron sputtering (HiPIMS) [1] and later in DC magnetron sputtering (DCMS) [2]. In DCMS discharges operated at low-currents and low-pressure a single ionization zone forms with the shape of an elongated arrowhead and rotates in the direction opposite to the electron drift (i.e., in the -**E**×**B** direction). In this work we used emissive and floating probes to measure plasma and floating potentials of rotating ionization zone for a magnetron with a 3" niobium target operated at 2 mTorr (0.27 Pa), -270 V and 100 mA. Both probes showed strong temporal and spatial variations of the signals. From the measurements in the radial and axial directions we reconstructed full three-dimensional distributions of the plasma potential. The potential distribution was compared with the images recorded by an intensified CCD camera. Strongest light intensities in the zone corresponded to maximum plasma potential (i.e., ~0 V for probe positioned over the racetrack and for axial distances above 5 mm), whereas weaker light intensities corresponded to negative potentials (e.g., -70 V for the probe positioned over the racetrack and 5 mm away from the cathode). The plasma potential distribution matches with a previously suggested potential hump model [3]. Sharp drops in the light intensity are associated with large potential gradients, which result in strong in-plane electric fields. The largest in-plane fields are found in the azimuthal direction at the edge of the ionization zone (up to 10 kV/m). Weaker electric fields also form in the radial direction. The presence of the in-plane electric fields changes the paradigm of predominantly axially-directed electric fields. From the plasma potential we calculated the space charge distribution. A double layer is present around the edge of the ionization zone with higher ion density inside the zone and higher electron density just behind the zone's edge. From the difference between the plasma and floating potentials we also reconstructed the three-dimensional distribution of electron temperature. Electrons have largest energies in the area of highest light intensity (i.e., inside the zone and close to the edge) whereas their energy decreases along the drift direction in correlation with the fading light intensity.

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Plasma Science and Technology
Room 104B - Session PS+2D-TuA

Plasma Processing for Nanomaterials and 2D Materials

Moderator: Sumit Agarwal, Colorado School of Mines

2:20pm **PS+2D-TuA1 Analysis of Microplasma Reduction of Aqueous Silver and Gold Salts to Colloidal Nanoparticles**, ***Caroline De Vos***, Université Libre de Bruxelles, Belgium; *M.J. Gordon,* University of California, Santa Barbara; *R.M. Sankaran,* Case Western Reserve University; *F. Reniers,* Université Libre de Bruxelles, Belgium

The remarkable stability of microplasmas at atmospheric pressure and their non-thermal operation facilitate the introduction of liquids such as water for water treatment, medical, and material applications. Recently, there has been interest in the reduction of metal salts in aqueous solutions by microplasmas to produce colloidal nanoparticles (NPs). It is generally accepted that some active species from the plasma react with the solution phase and either directly reduce the metal cation or produce a reducing species. However, it remains unclear how exactly the metal cation is reduced to produce NPs.

In this study, we carried out experiments to understand the formation of silver (Ag) and gold (Au) NPs from their respective metal salt precursors with or without stabilizing capping molecule by reactions at the interface of a microplasma and the aqueous solution phase. The NPs were characterized after synthesis by ultraviolet-visible (UV-vis) absorption spectroscopy and transmission electron microscopy (TEM), and the chemical composition of the solution was characterized before and after microplasma treatment by ionic conductivity, electrochemical potential, and UV-vis absorption spectroscopy.

Our results show that both Ag and Au NP formation are directly proportional to the plasma current and process time. The calculated reduction efficiency based on the number of electrons injected and the number of Ag^+ reduced is only ~50% while the reduction efficiency for the Au precursor was ~25%. Another difference between the two metals is that plasmon band for Au was found to increase even after the plasma treatment was stopped. This was corroborated by a measured decrease in the concentration of the Au complex, confirming that reduction continues to occur without the plasma, presumably because of a long-lived reducing species generated in solution.

Assuming electrons are the important charge carriers, electrons can reduce metal cations, but can also reduce water to form OH radicals which in turn react to form hydrogen peroxide (H_2O_2). H_2O_2 is known to be a weak reducing agent and could also reduce the metal salts but based on our experiments and reduction potentials, we believe that H_2O_2 could only induce the formation of Au NPs.

To gain more insight into the different mechanisms involved, the gas phase above the plasma-liquid system was analysed by optical emission spectroscopy (OES); a variety of species were observed (OH, O, H, NO, N_2) and ultimately linked to the reactions occurring in the liquid phase.

This work was supported by the Belgian Federal Government (IAP research project P7/34 – Physical Chemistry of Plasma Surface Interactions).

2:40pm **PS+2D-TuA2 Controllable Optical Properties of Plasmonic TiN Nanoparticles Synthesized by a Scalable Non-Thermal Plasma Method**, ***Alejandro Alvarez Barragan***, *L. Zhong, L. Mangolini,* University of California Riverside

Titanium nitride is a refractory material with optical properties similar to those of gold. It has therefore attracted significant interest, since TiN nanoparticles are expected to show localized surface plasmon resonance in the visible/near-infrared range, all while overcoming the cost and thermal stability limitations of gold. For instance, they are a very attractive substitute of gold nanoparticles in biomedical applications [1]. Most of the methods involving TiN nanopowder synthesis use effective but complicated chemical routes [2,3]. In this contribution, we present a highly scalable method for the production of TiN nanoparticles using a non-thermal plasma process. A low-pressure non-thermal plasma reactor is used to continuously nucleate and grow crystalline TiN nanoparticles starting from a mixture of ammonia and titanium tetrachloride. Besides achieving a remarkable production rate (~50 mg/h), we were also able to control the particle size and stoichiometry with great precision by tuning process parameters such as gas composition and plasma input power. This finding is of paramount importance because the plasmonic peak position is highly dependent on these two parameters [4]. Absorption measurements of the as-synthesized particles show clear plasmonic resonance in the near-infrared region, ranging between 800 and 1000nm when dealing with the largest and smallest particles, respectively. XRD and high resolution TEM/EDS characterization also provides insight on the nitrogen content of the samples and its close correlation to particle size. The role of process parameters on the surface of the particles, which in turn affects their plasmonic properties, will be discussed extensively.

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3:00pm **PS+2D-TuA3 Plasma Prize Talk: Nonthermal Plasma Synthesis of Nanocrystal Materials**, *N.J. Kramer, K. Schramke, T. Chen, H. Fu, S. Ehrenberg, K. Reich, B. Shklovskii,* ***Uwe Kortshagen***[*], University of Minnesota **INVITED**

Nonthermal plasma synthesis of nanocrystals is particularly suited for covalently bonded materials that require high temperatures to be produced with good crystallinity. Several years ago, we showed that plasma produced silicon nanocrystals are capable of high-efficiency photoluminescence, different from bulk silicon material. More recently, the capability of nonthermal plasmas to produce substitutionally doped nanocrystal materials has attracted attention, as substitutional doping had presented a significant challenge both for liquid and gas phase synthesis due to effects such as self-purification.

This presentation discusses the physics of plasma synthesis process. High photoluminescense quantum yields are achieved by careful surface functionalization through grafting alkene ligands to the nanocrystal surfaces. We also discuss the substitutional doping of silicon nanocrystals with boron and phosphorous using a nonthermal plasma technique. While the synthesis approach is identical in both cases, the activation behavior of these two dopants is found to be dramatically different. Finally, we present some experimental work on transport in films of highly phosphorous-doped nanocrystals, which indicates the approach to the metal-to-insulator transition.

This work was supported in part by the NSF Materials Research Science and Engineering Center under grant DMR-1420013, the DOE Energy Frontier Research Center for Advanced Solar Photophysics, and the Army Office of Research under MURI grant W911NF-12-1-0407.

4:20pm **PS+2D-TuA7 Initiated Plasma Enhanced Chemical Vapor Deposition of Metalloporphyrins: A Simple Route towards the Deposition of Metal Organic Covalent Networks**, ***Nicolas BOSCHER***, Luxembourg Institute of Science and Technology, Luxembourg; *M. WANG, K. GLEASON,* Massachusetts Institute of Technology

Porphyrins and porphyrinoids are robust and versatile functional molecules with varying properties depending on their central metal ion and peripheral and axial substituents. They have proved to be useful in a wide range of applications, including the catalysis and photocatalysis of various chemical reactions, in molecular sensing, light harvesting applications, and for gas storage and gas separation applications. In addition to these functional assets, their rigidity and chemical stability make them ideal as building units for the formation of covalent and coordination metal-organic polymers, including metal-organic frameworks (MOFs). Nevertheless, the difficult processability of these poorly soluble and non-meltable materials makes difficult their integration into smart devices.

Provided the fact that the monomer to deposit possesses free-radical polymerizable bonds, initiated PECVD (iPECVD) promotes conventional chain-growth polymerisation pathways, ensuring an excellent retention of the monomer structure. Several works have highlighted the radical

[*] **PSTD Plasma Prize**

polymerizability of the exo-pyrrole double bond of the porphyrin rings. The propagation reaction occurs at the beta-position of the porphyrin ring, leading to the formation of a polymer of reduced porphyrins, i.e. chlorin. Based on this wet-chemistry result, we recently investigated the use of zinc (II) meso-tetraphenylporphyrin (ZnTPP) building units in an iPECVD process and formed a new kind of metal-organic covalent network (MOCN) thin films.

5:00pm **PS+2D-TuA9 Plasma-graphene Interaction and its Effects on Nanoscale Patterning**, *A. Harpale,* University of Illinois at Urbana-Champaign; ***Huck Beng Chew,*** University of Illinois at Urbana Champaign **INVITED**

Graphene is the lightest and strongest known material, and is also an ideal thermal and electrical conductor. Despite its unique properties, graphene has to be patterned to achieve its full engineering and nanotechnological potential. Recent experiments show that a monolayer of graphene deposited on an SiO2 substrate and subjected to hydrogen plasma treatment either undergoes (a) selective etching from the edges of the graphene sheet while leaving the basal plane intact, or experiences (b) etching of both the edges and basal plane of the graphene sheet which results in the formation of nanoscale holes in graphene. The plasma-etched holes in (b) can be either circular or hexagonal, suggesting that the etching process can be isotropic or anisotropic. Here, we model the hydrogen-plasma etching of monolayer graphene on SiO2 substrates across the range of plasma energies using scale-bridging molecular dynamics simulations. Our results uncover distinct etching mechanisms, operative within narrow hydrogen-plasma energy windows, which fully explain the differing plasma-graphene reactions observed experimentally. Specifically, our simulations reveal very sharp transitions in the etching mechanisms with increasing hydrogen ion energy: selective edge etching at ion energies of ~1 eV, isotropic basal plane etching at ion energies of between 2 and 5 eV, and anisotropic etching at ion energies > 7 eV. Understanding the complex plasma-graphene chemistry and the relationship to plasma process parameters opens up a means for controlled patterning of graphene nanostructures.

5:40pm **PS+2D-TuA11 A Closer Look at Chemically Modified Graphene**, ***Sandra Hernández,*** Naval Research Laboratory **INVITED**

Graphene has been a research focus due to its numerous unique properties which have motivated vast interdisciplinary research in the search of materials for next-generation technologies. With its unique atomically thin nature, graphene has enabled a closer look at material surface interactions and highlighted the importance of surface interfaces, defects and adsorbates. Purposeful and native defects have demonstrated to have advantageous or adverse influences on the chemical, electrical, optical, mechanical and even magnetic properties of graphene. On the other hand, control of the localization of defects and their arrangement onto ordered and extended structures has enabled new graphene-based materials with novel properties. Surface functionalization has provided the ability to manipulate the material attributes, offering a range of opportunities for the chemically modified materials. It is clear that fundamental understanding of the modification of graphene relies on the understanding of the chemical functionalization dynamics, kinetic barriers, chemical transitions, and diffusion energies experienced by the added adsorbates with the graphene surface as well as the influence of the substrate on each.

Plasmas provide both ease and versatility by enabling a single tool process on a wide range of background gases. In particular, electron-beam generated plasmas can introduce different functional groups over a large coverage range with atomic layer precision, providing the ability to tailor the locality of the surface chemistry on graphene opening up a wide range of reactivity studies and synthesis capabilities. Such unique ability allows for precise nano-engineering of the surface chemistry effecting local electronic properties, electron transfer kinetics, and surface reactivity; opening up a wealth of opportunities in device performance, chemical sensing, bottom-up material growth, plasmonics, and catalysis applications.

This work is supported by the Naval Research Laboratory Base Program.

Plasma Science and Technology
Room 104C - Session PS+TF-WeM

Atomic Layer Etching

Moderator: Eric A. Hudson, Lam Research Corporation

8:00am **PS+TF-WeM1 Selective Cyclic Plasma Etching of Thin Films in Two Heating Way, Ion Bombardment and Infrared Irradiation.**, *M. Izawa,* Hitachi High-Technologies Corp., Japan*;* ***Kazunori Shinoda****, N. Miyoshi, H. Kobayashi,* Hitachi, Japan*; N. Yasui, M. Tanaka, Y. Sonoda, K. Kuwahara,* Hitachi High-Technologies Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan **INVITED**

With shrinking device size and introduction of 3D FinFET transistor structure, cyclic Atomic Layer Etching (ALEt) becomes one of the key technologies in thin film etch. To achieve extreme high selectivity against mask and etch-stop layers, atomic level etching as a method to meet these etching requirements and eliminate physical damage has been investigated. Further, isotropic ALEt will be required for use in nanoscale patterning for formation of more complex 3D structures. In cyclic ALE technology, a modification layer is formed on a thin film layer by supplying etching species. After that, the modification layer is removed by heating. We investigated two types of ALEt tools; one is a anisotropic ALE tool based on Microwave ECR plasma and the other is a isotropic ALE based on ICP type down-flow plasma.

Recently, we have reported results of isotropic ALEt of Silicon Nitride (SiN) film [1]. High-throughput and high-selectivity ALEt of SiN using IR irradiation and down-flow plasma was also demonstrated [2]. Modification layer, ammonium hexafluorosilicate ($(NH_4)_2SiF_6$), was synthesized by fluorocarbon gas plasma and nitrogen supplied from SiN flim. Because the modification layer is formed only on SiN film, SiN film can be removed with high selectivity at IR radiation heating step. This technology can be also applicable to ALEt of TiN.

Anisotropic ALEt was also investigated by using Microwave-ECR plasma [3]. In this study, Ar ion irradiation was utilized instead of heating. To achieve high selectivity, the ion energy lower than sputtering threshold is required. Because microwave-ECR plasma has low plasma potential and is not fluctuated by wafer RF power, lower ion energy is available. In addition, It is known that excessive dissociation of gases and by-products causes reverse reaction and degradation of selectivity. We therefore used high gas flow rate and pulsed plasma to reduce dissociation. This ALEt technology has been applied to high selective etching of Si, HfO_2, and SiN film.

[1] K. Shinoda *et al*., AVS Atomic Layer Etching workshop 2015.

[2] N. Miyoshi *et al*., 62 nd AVS, , PS+SS+TF-WeM5, 2015.

[3] M.Tanaka *et al*. , SPIE Advanced Litho., 9428-23, 2015.

8:40am **PS+TF-WeM3 Concurrent Engineering of Atomic Layer Etch Patterning Processes Involving Oxide and Nitride Materials**, ***Mingmei Wang****, P. Chan,* TEL Technology Center, America, LLC*; P. Ventzek,* Tokyo Electron America*; A. Ranjan,* TEL Technology Center, America, LLC

Atomic layer etching (ALE) of Si has been the focus of extensive research and development for over two decades. [1] However, the precision etch of dielectric materials (SiO_2, Si_3N_4) in patterning schemes employing self-aligned contacts (SACs) and self-aligned multiple patterning (SAMP) at the 10nm technology node and beyond are where ALE has significant potential. In both SAC and SAMP schemes, an oxide layer must be etched selective to a thin nitride layer with a corner with a thickness and radius of curvature of less than 10 nm. Fortunately precision etch using cyclic deposition/etch schemes have been proven effective at preserving the thin nitride corner. Unlike atomic layer etching of silicon using chlorine, fluorocarbon chemistry etching of nitride and oxide is not self-limiting process. The thin fluorocarbon polymer layers that protect the nitride layer corner deep in a feature are difficult to measure with common in-line metrology. Both these facts make trial-and-error development of processes for cyclic etch of oxide materials selective to nitride underlayers challenging. We have used concurrent engineering approaches including both modeling and experiment to bypass these difficulties. The core of the approach is a new integrated chamber (HPEM)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [2] for oxide nitride etch experiments conducted on a dual frequency plasma source using a benchmark $Ar/C_4F_6/O_2$ chemistry. The concurrent engineering approach comprises stages of development and prediction tests using both blanket wafer and patterned coupon data and finally process parameter optimization. By using this approach, we have minimized nitride corner loss and optimized nitride/oxide etch selectivity with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a case study in SAC process development. Furthermore, insights into the relationship between chamber function and critical surface processes will be discussed.

[1] A.Ranjan, M.Wang, S.Sherpa, V. Rastogi, A. Koshiishi, and P.Ventzek, J. Vac. Sci. Technol. A34, 2016.

[2] M.Wang and M.Kushner, J. Appl. Phys 107, 2010.

9:00am **PS+TF-WeM4 System Trade-offs of Atomic Layer Etching (ALE) of High Aspect Ratio 3D Features**, ***Chad Huard****,* University of Michigan*; Y. Zhang, S. Sriraman, A. Paterson,* Lam Research Corp.*; M.J. Kushner,* University of Michigan

Atomic layer etching (ALE) is a method for decoupling process parameters that, with continuous etching, are usually difficult to separately control. ALE does so at the trade-off of decreased etch rate. Of particular interest is the ability of ALE to separate the consequences of plasma parameters, such as ion to neutral flux ratios and ion energies, from issues of transport into and out of the feature. By using separate and self-limited reactions for surface passivation and material removal, ALE offers a way to deliver the optimum neutral/ion ratio at any aspect ratio at the trade-off of increasing etch time.

Using a 3-dimensional voxel based Monte-Carlo feature profile model, the trade-off between etch time and etch fidelity encountered in the ALE regime has been investigated. The poly-silicon gate etch process of a high-k metal replacement finFET is the base case for this study. The time-multiplexed scheme to achieve ALE is an Ar/Cl_2 plasma passivation step followed by an Ar plasma step having higher ion energies to remove Si. We found that the change in neutral conductance of the feature as the aspect ratio increases requires adjusting process step times to optimize etch rates. We also found that ALE is able to clear corners in 3D features more effectively than continuous etching, requiring less over-etch. A measure of clearing efficiency is the amount of over-etch required to clear the corners compared to the total etch time. The clearing efficiency was investigated for an entirely ALE process and a hybrid approach using a continuous main etch followed by an ALE clearing etch, over a range of geometries including varying fin spacing and side-wall slope.

Work was supported by Lam Research Corp., Department of Energy Office of Fusion Energy Science and the National Science Foundation.

9:20am **PS+TF-WeM5 Molecular Dynamics Simulations of Atomic Layer Etching**, ***Jun-Chieh Wang****, S. Rauf, J.A. Kenney, L. Dorf, K.S. Collins,* Applied Materials, Inc. **INVITED**

Sub-nm precision is increasingly being required of many critical plasma etching processes in the semiconductor industry. As such, atomic layer etching (ALE) has become a potential candidate for accurate control of a variety of critical etching processes. In ALE, the target substrate is first exposed to a reactive gas that passivates the surface followed by ion bombardment with energy below the sputtering threshold. It is essential to precisely control the ion/radical energy and flux during the etching process to remove the topmost passivated surface without damaging the underlying substrate. Once the passivation layer is removed, the etch process stops. The passivation and etching steps repeat until one has etched to the desired thickness. In contrast to conventional radio-frequency (RF) plasma etching processes, microfabrication using ALE promises high selectivity and low damage to the substrate. In this talk, we discuss the properties of ALE on a patterned surface using results from molecular dynamics (MD) simulations. A chlorinated Si/SiO2 surface was bombarded by Ar^+ or Cl^+ ions to remove the modified surface layers. With Ar^+ energy below the sputtering threshold, etch process stops after the Si surface becomes deficient in Cl atoms; while at high bombarding energy, Si removal continuous with lower rate partly due to physical sputtering. For Cl^+ ion bombardments, the Si surface is continuously etched at a constant rate, and the etch rate increases with Cl^+ ion energy. Results for different aspect ratios will also be discussed. These fundamental studies are used to interpret our layer-by-layer ALE experiments.

11:00am **PS+TF-WeM10 Isotropic Atomic Layer Etching of Titanium Nitride Using Formation and Desorption of Ammonium Salt**, ***Kazunori Shinoda****, N. Miyoshi, H. Kobayashi, M. Kurihara,* Hitachi, Japan*; S. Sakai, M. Izawa,* Hitachi High-Technologies, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

There is growing interest in atomic layer etching (ALEt) as 3D devices become widely used and feature sizes continue to scale down. The

development of isotropic ALEt for various materials will be important for existing and future 3D devices such as a 3D NAND, Fin FET, and GAA FET. Recently, the authors developed an isotropic ALEt for SiN using formation and desorption of an ammonium hexafluorosilicate-based modified layer [1]. High-throughput high-selectivity ALEt of SiN using IR irradiation was also demonstrated by the authors [2]. In this work, isotropic ALEt of TiN using formation and desorption of an ammonium salt-based modified layer is developed.

The experimental apparatus used in this study is composed of a reaction chamber and an x-ray photoelectron spectroscopy (XPS). TiN deposited by atomic layer deposition was used as the sample material. Several samples were exposed to radicals that were generated in fluorocarbon-based gas mixtures. The samples were then annealed by using circulating fluid. The surface of the samples was analyzed by XPS. Photoemission spectra obtained after radical exposure and after thermal annealing of the TiN samples are compared. The etching depth was evaluated by ellipsometry.

A nitrogen 1s peak (402 eV), which has been assigned as ammonium salt, was observed after radical exposure. Titanium 2p peaks (462 and 467 eV), which originate from a Ti-F bond, were observed simultaneously. These results imply that the surface of the radical exposed TiN consists mainly of ammonium salt such as ammonium fluorotitanate. After the samples were annealed on the wafer stage heated at 210°C, the nitrogen 1s peak at 402 eV, which is assigned as ammonium salt, disappeared. A nitrogen 1s peak at 396 eV, which is attributed to TiN, appeared after the ammonium salt-related peak disappeared. This phenomenon implies that the film of ammonium salt decomposed and desorbed from the TiN surfaces at elevated temperatures.

The preliminary tests of cyclic etching are carried out by repeating radical exposure and thermal annealing. For one cycle of etching, the etching depth increases with increasing radical exposure time and saturates at 0.7 nm. For multiple cycle etching, the etching depth increases with an increasing number of repetitions of the cycle. Tuning of the etched amount per cycle (EPC) in the range from 0.3 to 0.7 nm was demonstrated by changing the composition of gas mixtures. From these results, it is concluded that the ALEt of TiN was successfully demonstrated.

[1] K. Shinoda et al., Atomic Layer Etching Workshop 2015, July 1–2, p. 572 (2015).

[2] N. Miyoshi et al., AVS 62nd International Symposium & Exhibition, PS+SS+TF-WeM5 (2015).

11:20am **PS+TF-WeM11 Organic Etchants Toward Atomic Layer Etching of Magnetic Metals**, ***Nicholas Altieri***, *L. Minardi, E.L. Chen, J.P. Chang,* University of California Los Angeles

The continued advancement in logic and memory devices relies heavily on the introduction of new materials. Of specific interest in the field of memory application is the utilization of magnetic metals and alloys such as Co, Fe, and CoFe as well as additional doped alloys such as CoFeB. Contemporary techniques for patterning these materials rely on noble ion beam milling which, although effective, leaves much to be desired in achieving selectivity and retaining pattern transfer fidelity for high aspect ratio features. One solution is the pursuit of atomic layer etching through reversal of the atomic layer deposition scheme and generation of volatile metal-organic species reminiscent of ALD precursors. Due to the etch-resistant nature of the materials studied, removal at an atomic level is enabled by chemical modification of the surface through plasma exposure and subsequent introduction of organic ligands.

Selected single element Co and Fe films as well as the magnetic metal alloy CoFeB (30nm) were studied using this scheme. Organic chemistries, such as acetylacetone (acac) and hexafluoroacetylacetone (hfac) were first investigated to determine the feasibility of metal-organic formation through direct exposure. The efficacy of acetylacetone and hexafluoroacetylacetone etching chemistries were confirmed through previous solution-based studies on Co and Fe, respectively, via formation of $Co(acac)_2$ (257 amu) and $Fe(hfac)_3$ (680 amu) as confirmed through mass spectrometry. Use of these organics was extended to the boron-doped alloy in the form mixtures with volumetric ratios of 1:3, 1:1, and 3:1 (acac:hfac). $Co_{30}Fe_{45}B_{25}$ was shown to etch at rates up to 15 nm/min in the 1:1 solution and ~1 nm/min at an organic mixture partial pressure of 60 Torr. The composition of the film as well as its metallic nature were preserved as seen by x-ray photoelectron spectroscopy (XPS) through the detection of Co and Fe metallic peaks present at 778.2 and 706.7 eV, respectively.

Chemical modification of the surface was then investigated as a means of controlling the amount of material removed and determining effects on material properties under various process conditions. XPS analysis of Co and Fe films processed under O_2 plasma show increasing thickness of CoO and Fe_2O_3 up to 3.7nm and 4.6nm, respectively after 5 min exposure. Magnetic properties of both single element and alloyed films were characterized using superconducting quantum interference device magnetometry (SQUID) and displayed degraded magnetic properties through increasing coercivity with increasing oxidation time.

11:40am **PS+TF-WeM12 Conformality of Thermal Al_2O_3 Atomic Layer Etching in High Aspect Ratio Structures**, ***Amy Marquardt***, *H. Sun,* University of Colorado Boulder*; S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) is the reverse of atomic layer deposition (ALD). Conformal deposition in high aspect ratio structures is one of the key features of ALD. The conformality of etching in high aspect ratio structures will also be important for thermal ALE. In this study, the conformality of thermal Al_2O_3 ALE was investigated in channels with high aspect ratios ranging from 60 to 200. Al_2O_3 ALD was used to deposit the initial Al_2O_3 films in the channels. The Al_2O_3 ALE was performed at 300°C using HF and $Al(CH_3)_3$ as the reactants. HF is known to fluorinate Al_2O_3 and form an AlF_3 layer on the Al_2O_3 surface. The $Al(CH_3)_3$ then undergoes a ligand-exchange transmetalation reaction with the AlF_3 layer. $Al(CH_3)_3$ accepts fluorine and donates methyl ligands to the surface. This ligand-exchange allows the Al in the AlF_3 layer to leave as a volatile reaction product such as $AlF(CH_3)_2$ or $Al(CH_3)_3$. The conformality of Al_2O_3 etching was examined in high aspect ratio channels defined by stainless steel foil spacers between silicon substrates. Spectroscopic ellipsometry was used to measure the Al_2O_3 film thickness in the channels. Increasing the aspect ratio increased the reactant exposure and purge times necessary to maintain conformal etching. Longer times were required to allow the reactants and products to diffuse in and out of the high aspect ratio channels. Increasing the reactant pressures also lowered the required reactant exposure times. However, increasing the reactant pressures from 0.1 to 9 Torr also increased the Al_2O_3 etching rate. The higher etching rates were attributed to a thicker AlF_3 layer formed at higher reactant partial pressures. Using longer reactant exposure or purge times or higher reactant pressures, conformal Al_2O_3 etching was obtained in the high aspect ratio channels.

12:00pm **PS+TF-WeM13 Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas**, ***Nicholas Johnon***, *H. Sun, K. Sharma, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) has been recently demonstrated for a variety of oxides such as Al_2O_3, HfO_2 and ZrO_2 using sequential, self-limiting fluorination and ligand-exchange reactions. In this work, the thermal ALE of aluminum nitride, a III-V metal nitride, was performed for the first time. Crystalline aluminum nitride (AlN) films were etched using hydrogen fluoride (HF) and tin(II) acetylacetonate ($Sn(acac)_2$) as the reactants. The AlN films were in the crystalline wurtzite phase with the (0001) plane parallel to the surface. Film thicknesses were monitored versus number of ALE reaction cycles at 275°C using in situ spectroscopic ellipsometry (SE). A low etch rate of 0.07 Å/cycle was measured during etching of the first 40 Å of the film. These small etch rates corresponded with the AlO_xN_y layer on the AlN film. The etch rate then increased to 0.36 Å/cycle for the AlN films. In situ SE experiments established the HF and $Sn(acac)_2$ exposures that were necessary for self-limiting surface reactions. In the proposed reaction mechanism for thermal AlN ALE, HF fluorinates the AlN and produces an AlF_3 layer on the surface. The metal precursor, $Sn(acac)_2$, then accepts fluorine from the AlF_3 layer and transfers an acac ligand to the AlF_3 layer in a ligand-exchange reaction. The volatile etch products are SnF(acac) and either $Al(acac)_3$ or $AlF(acac)_2$. Adding a H_2 or Ar plasma exposure to the reaction sequence enhanced the etching rates. A H_2 or Ar plasma exposure after the $Sn(acac)_2$ exposure increased the AlN etch rate from 0.36 Å/cycle to 1.96 Å/cycle or 0.9 Å/cycle, respectively, at 275°C. The enhanced etch rates are believed to result from either H radicals or photons from the H_2 plasma or ions or photons from the Ar plasma. The H radicals may be able to remove acac surface species that may limit the etch rate. The photons or ions may also lead to the desorption of surface species or substrate excitation that enhances the etch rate.

Plasma Science and Technology
Room 104B - Session PS-WeM

Plasma Sources and Novel Mechanisms for Generating Plasmas

Moderator: Sumit Agarwal, Colorado School of Mines

8:00am **PS-WeM1 Multifrequency Impedance Matching Solutions for Plasma Excitation by Tailored Voltage Waveforms**, ***Erik V. Johnson,*** Ecole Polytechnique, Palaiseau, France*; S. Dine,* SOLAYL SAS, France*; J.-P. Booth,* Ecole Polytechnique, Palaiseau, France

Tailored Voltage Waveforms (TVWs) and the Electrical Asymmetry Effect they induce in plasmas are useful tools to both optimize plasma processes and gain insight into the role of specific plasma parameters (ion bombardment energy, species flux) in processing outcomes. However, the multi-frequency nature of these waveforms, which are composed of a fundamental frequency in the MHz range and a number of its harmonics (e.g. 13.56MHz + 27.12MHz + 40.68MHz….), leads to a practical technical challenge, namely multi-harmonic impedance matching. Although impedance matching the 50 ohm output of an amplifier to a plasma processing chamber with a large reactive component is easily achieved for a single frequency using a passive component matchbox, doing the same at multiple harmonics is much more challenging due to the frequency response of every circuit element (including the chamber).

One strategy that has been employed and deployed as a commercial product is the use of multiple amplifiers, matchboxes, and filter sets, one for each frequency used. Although technically effective, using individual amplifiers for each frequency may not be the most cost-effective solution. Alternatively, we have previously proposed a technique to simultaneously match at multiple frequencies using a passive multi-frequency matchbox (MFMB), but this minimal-component solution is difficult to control due to variations in components affecting the response at pairs of frequencies.

In this work, we present results from a new design of MFMB using only passive components. Critically, this new design allows (1) independent control of the frequency response at each harmonic, and (2) the use of a single high-power amplifier. Circuit simulation results as well as experimental results are shown for a small area, laboratory plasma processing chamber during an argon plasma for three-frequency operation, and for fundamental frequencies between 9 and 15 MHz. It is demonstrated that although adjusting the matching condition for the fundamental frequency (1f) changes the matching for the other two (2f, 3f), the converse is not true; adjusting the matching on the higher harmonics does not impact that of the fundamental. Furthermore, we show that this improved matching is indeed due to better power transfer and not parasitic losses in the matching network.

8:20am **PS-WeM2 Effect of Tailored Voltage Waveforms on Surface Nanotexturing of Silicon in Capacitively Coupled SF_6/O_2 Discharges**, ***Guillaume Fischer,*** Institut Photovoltaïque d'Ile-de-France (IPVF), France*; E. Drahi, G. Poulain,* Total MS-Energies Nouvelles, France*; B. Bruneau, E.V. Johnson,* LPICM, Ecole Polytechnique, France

The nanotexturing of the surface of a crystalline silicon (c-Si) wafer for improved photovoltaic performance can be achieved through the use of an SF_6/O_2 reactive ion etching (RIE) capacitively coupled plasma (CCP). The resulting surfaces typically consist of nano-sized structures resembling cones (sizes ranging from 30 to 500nm) with little preferential crystallographic orientation. The process occurs through competing mechanisms involving Si etching by fluorine radicals, formation of in-situ micro-masking species, and physical etching by ions, all these mechanisms being strongly influenced by plasma conditions.

As has been done for previous processes and chemistries, we attempt to decouple the influence of various plasma properties through the use of Tailored Voltage Waveforms (TVWs), and thus obtain insights into the mechanisms involved in the dry nanotexturing of silicon. TVW excitation consists of adding harmonic frequencies with controlled amplitudes and phase-shifts to the RF (13.56 MHz) driving voltage, and allows one to quasi-independently control parameters such as species flux and ion bombardment energy (IBE). Furthermore, in an electronegative chemistry such as the SF_6/O_2 mixture, waveforms resembling "sawtooths" induce high ionization asymmetries due to plasma sheath dynamics, and may impact the type of reactive species arriving at the surface.

In this study, the phase-shift of the harmonic frequencies of the TVW excitation is varied at constant discharge power in an SF_6/O_2 mixture, therefore modifying (by an up to fourfold increase in absolute value) the self-bias voltage (V_{DC}) at the powered substrate holder and therefore the maximum IBE. The impact of varying the TVW shape is observed through both the plasma properties (V_{DC}, optical emission) and the morphological and optical properties of the obtained nanotexture. The effectiveness of the texture is quantified by the surface effective reflectance (R_{eff}) which is the average reflectance weighted by the solar spectrum irradiance.

It is here shown that the use of TVW excitation allows, at constant discharge power, to switch from a regime with no etching (almost no change of R_{eff}, no nanostructures observed) to a texturing regime where the decrease of R_{eff} scales with the IBE (R_{eff} decreasing up to 30% and nanocones observed). Moreover, new types of nanostructures have been observed for some particular etching regimes, showing partial dependence on the crystallographic orientation of the substrate.

8:40am **PS-WeM3 Plasma Enhanced CVD processes: Dual Frequency PECVD with pulsing of liquid precursors and PEALD for Selective Deposition**, ***Christophe Vallee,*** LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R. Gassilloud,* CEA, LETI, MINATEC Campus*; R. vallat,* LTM, Univ. Grenoble Alpes, CEA-LETI*; F. Piallat,* Altatech, France*; M. Aoukar,* LTM, Univ. Grenoble Alpes, CEA-LETI*; P. Kowalczyk,* LTM - CEA/LETI, France*; P.D. Szkutnik,* LTM, Univ. Grenoble Alpes, CEA-LETI*; P. Noé,* CEA, LETI, MINATEC Campus*; A. Bsiesy, P. Gonon,* LTM, Univ. Grenoble Alpes, CEA-LETI **INVITED**

With this presentation we will address two topics concerning the development of specific Plasma Enhanced CVD processes for microelectronics applications: Dual Frequency (DF) with pulsed liquid injection of precursors and selective deposition.

First, we will talk about Dual Frequency processes for PECVD applications. Since the excitation frequency has extensive effects on the spatial distribution of species and their concentrations, the dissociation of the precursor can also be increased by crossing the discharge excitation frequency to the basic ion plasma frequency. This route is considered here with comparison and discussion over the improvements brought by Dual Frequency LF/RF plasmas in the case of thin metal gate (TiN) and Phase Change Material (GeSbTe) deposition. For this study we used 200 mm and 300 mm commercial PECVD tools from Altatech with a pulsed liquid injection of precursors. We will show that during TiN deposition the plasma enters a g-mode due to secondary electron heating. Then adding LF to RF modifies the sheath thickness of the plasma, increases the electron temperature of the gas and thus leads to strong modification of the carbon content, density and growth rate. For PCM applications, very different cycles (amorphous to crystalline) are obtained for GeTe materials elaborated in RF mode or DF mode. Moreover, we observe a very strong improvement of the gap filling capability of the process by using the DF mode.

The second part of this talk will be dedicated to the development of a selective deposition process by PEALD. One of the main challenges brought by the reduction of the transistor size below 10 nm is the development of selective deposition processes (for a self-forming Cu diffusion barrier for example). ALD is a suitable technique for selective deposition since it is a self-limited surface reaction process. The resulting selective process, called SeALD (Selective ALD) or AS-ALD (Area Selective ALD) is usually based on a specific surface treatment before deposition. Indeed, in ALD process, thin film nucleation depends strongly on the surface chemistry, so that by using a specific treatment one can transform a chemically reactive site into a nonreactive one. In this part, we propose a new selective ALD process, without surface treatment before deposition but using a Plasma assistance ALD process and by playing on the plasma chemistry. We will show for example that we are able to deposit selectively Ta_2O_5 oxide on top of metal (TiN) while no deposition is obtained on Si or SiO_2 surfaces. The process and its potential application will be described in more details during the talk.

9:20am **PS-WeM5 Customizing Ion Energy Distributions in Pulsed Plasmas with Chirped Bias Power**, ***Steven Lanham,*** *M.J. Kushner,* University of Michigan

Control of the ion energy distribution (IED) in plasma material processing reactors is necessary to maintain the critical dimensions (CD) needed to produce modern microelectronic devices. An effective way to customize IEDs is using pulsed power. For example, electronegative (e.g. halogen) plasmas used in etching processes form ion-ion plasmas during the power off period, where low energy ions can be preferentially extracted. This also allows for extraction of negative ions during the afterglow, which can help negate charge induced damage. Pulsed power parameters such as duty cycle and pulse repetition frequency need to be optimized for different electronegative plasmas chemistries due to varying attachment rates and

heavy particle reaction mechanisms. The choice of frequency for the bias is a first-order decision in forming the IED, even in pulsed systems, which has in turn resulted in multi-frequency biases to aid in further customization. The use of multi-frequency biases brings additional complexity to pulsed systems.

In this work, based on a computational investigation, we discuss methods to produce customized IEDs in pulsed, electronegative inductively coupled plasmas. A 2-dimensional model, the Hybrid Plasma Equipment Model (HPEM), was used for this study. For pulsed biases in inductively coupled plasmas, IEDs will be discussed for various halogen plasma chemistries. Chirped biases in which the frequency is ramped during a pulsed period are discussed as a means to replicate IEDs that can otherwise only be formed in dual or triple frequency systems.

Work was supported by the Department of Energy Office of Fusion Energy Science and the National Science Foundation.

9:40am **PS-WeM6 Nonlinear Frequency Pull in Pulsed Capacitively Coupled Plasmas**, *J. Poulose,* ***Lawrence Overzet****, M.J. Goeckner,* The University of Texas at Dallas*; S. Shannon,* North Carolina State University*; D. Coumou,* MKS Instruments

Plasma ignition induces abrupt impedance changes due to the plasma sheath and bulk formation. These transitions can induce nonlinear changes in the instantaneous RF voltage and current frequencies despite the fact that the RF frequency is typically assumed to be fixed. These transitions are of particular interest in the application of frequency tuning of matching networks to maximize power transfer in pulsed plasma. In this presentation, we report on time resolved studies of the RF frequency and plasma impedance during pulsed plasma ignition using both electropositive (Ar) and electronegative (CF4/O2/Ar) gas mixtures. The center frequency is found to vary in time corresponding to fast changes in the complex plasma impedance when the plasma sheath is re-forming.

11:00am **PS-WeM10 Plasma Source Development for Fusion Relevant Material Testing**, ***John Caughman****, R.H. Goulding, T.M. Biewer, T.S. Bigelow, I.H. Campbell, S.J. Diem, A. Fadnek, D.T. Fehling, D.L. Green, C.H. Lau, E.H. Martin, P.V. Pesavento, J. Rapp,* Oak Ridge National Laboratory*; H.B. Ray, G.C. Shaw, M.A. Showers,* University of Tennessee*; P. Piotrowicz, D.N. Ruzic,* University of Illinois at Urbana-Champaign*; G.-N. Luo,* Chinese Academy of Sciences **INVITED**

Plasma facing materials in a magnetic fusion reactor have to tolerate plasma heat fluxes of 10 MW/m^2. The Prototype Materials Plasma Experiment (Proto-MPEX) is a linear high-intensity radio frequency (RF) plasma source that combines a high-density helicon plasma generator with electron and ion heating sections. It is being used to study the physics of heating over-dense plasmas in a linear configuration with the goal of producing up to 10 MW/m^2 of plasma heat flux on a target. The helicon plasma is operated at 13.56 MHz with RF power levels up to 100 kW. Microwaves at 28 GHz (~150 kW) are coupled to the electrons in the over-dense helicon plasma via Electron Bernstein Waves (EBW), and ion cyclotron heating (~30 kW) is via a magnetic beach approach. Plasma diagnostics include Thomson Scattering and a retarding field energy analyzer near the target, while a microwave interferometer and double-Langmuir probes are used to determine plasma parameters elsewhere in the system. Filterscopes are being used to measure D-alpha emission and He line ratios at multiple locations within the device, and IR cameras image the target plates to determine heat deposition both upstream and downstream of the helicon source region. High plasma densities have been produced in helium (>3x10^{19}/m^3) and deuterium (>2x10^{19}/m^3), with electron temperatures that can range from 2 to >10 eV. Operation with on-axis magnetic field strengths between 0.6 and 1.4 T is typical. The plasma heat flux delivered to a target can be > 10 MW/m2, depending on the operating conditions. Plasma parameters vary depending on the operating pressure/gas flow, and skimmer plates are used to try to control the neutral pressure in the device. The ion energy distribution varies radially/axially and is related to changes in the electron temperature and antenna coupling conditions. The helicon antenna coupling is being model with the COMSOL and VORPAL programs to help explain and guide operations. Details of the experimental results and operating parameters related to ion energies and delivered plasma heat flux will be presented.

11:40am **PS-WeM12 Linear Magnetron Magnet Pack for High Power Pulsed Magnetron Sputtering**, ***Jake McLain****, P. Raman, I.A. Shchelkanov,* University of Illinois at Urbana Champaign*; J. Hrebik,* Kurt J. Lesker Company*; B. Jurczyk, R. Stubbers,* Starfire Industries*; D.N. Ruzic,* University of Illinois at Urbana-Champaign

High Power Pulsed Magnetron Sputtering (HPPMS) is an ionized physical vapor deposition technique that utilizes high power pulses applied to the sputtering target. The high power densities allow for an increased percentage of sputtered particles to be ions, and the ions allow for more control over the deposition process. The enhanced control allows for improved film quality and surface adhesion when compared with DC magnetron sputtering (DCMS). The primary reason for the lack of industrial implementation is the intrinsically low deposition rate that HPPMS provides. The Center for Plasma-Material Interactions has designed a high deposition rate HPPMS magnet pack that produced comparable deposition rates in HPPMS when compared with a conventional magnet pack using DCMS for a 4-inch circular magnetron with a titanium target at 500W. This magnet pack also increased the HPPMS deposition rate twofold when compared with the conventional magnet pack using HPPMS [1]. To allow for industrial implementation of HPPMS, a similar high deposition rate magnet pack is designed and built for a linear magnetron, capable of being scaled to any desired length. This work focuses on the similarities and differences in the process and physics of the standard and new magnet packs. The properties explored in this work include deposition rate, deposition uniformity, plasma parameters, and film quality.

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Plasma Science and Technology
Room 104B - Session PS+TF-WeA

Plasma Deposition and Plasma Assisted ALD

Moderators: Noemi Leick, Colorado School of Mines, Adrie Mackus, Eindhoven University, Netherlands

2:20pm **PS+TF-WeA1 High Quality Film and Interface Formation using Appropriate Reaction Species**, ***Akinobu Teramoto,*** Tohoku University, Japan **INVITED**

The strong reactive species are required for the high quality film deposition by CVD or ALD. For oxides or nitrides formation, oxygen radicals or nitrogen radicals generated by the microwave exited plasma are very effective(1-3) because of high density and low plasma damages. The integrity of SiO_2 film formed by the microwave exited PECVD is the same as that formed by the thermal oxidation on Si(100) surface, and is superior than that formed by the thermal oxidation on any other surface of Si(100)(1, 2). The SiO_2 deposition rate of the microwave PECVD is sufficiently large for the practical use. For the SiNx film formation, the microwave PECVD is also effective. The quality of SiNx film formed by the PECVD at 400 °C is the same as that formed by thermal CVD(4, 5). However, the relatively long deposition time is required for high quality film deposition, and relatively low pressure is also required, as a result, the gap fill characteristics is weaker than the thermal CVD. The high quality SiNx film deposition at low temperature and relatively high pressure are required. The nitrogen radical generated by the atmospheric pressure discharge is attractive for these applications(6, 7).

We have to choose the reactive species more carefully when the depositing material is different from the substrate, such as Al_2O_3 on Si or GaN, SiO_2 on GaN. If the reactive species is excessively active, the species react not only the precursor but also the substrate, and the materials of the substrate and the film are mixed at the film/substrate interface, as a result, those mixed materials make defects and interface traps. Al_2O_3 can works as the gate insulator for the GaN-based MOSFET(8, 9) because of the large band gap and the high resistivity to Ga diffusion. The H_2O which has relatively lower oxidation ability than oxygen radical was used as the oxidant at the initial stage of Al_2O_3 ALD for suppressing the oxidation of GaN surface. Following radical oxygen treatment by microwave exited plasma is very effective for improving the film quality of Al_2O_3(9). It is noticed that the oxidation of GaN at the Al_2O_3/GaN interface must not occur during the oxygen treatment.

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3:00pm **PS+TF-WeA3 The Synergy of Diamond-like Carbon Film PECVD Systems: Plasma Diagnostics and Film Properties**, ***Tara Van Surksum,*** *E.R. Fisher,* Colorado State University

Diamond-like carbon (DLC) films have numerous potential applications because of their appealing mechanical and electronic properties (e.g., hardness, thermal conductivity, and high electrical resistance). Plasma enhanced chemical vapor deposition (PECVD) is a widely used technique in the production of DLC films, but to date, little is known about the underlying molecular-level chemistry involved in DLC plasma processing. In particular, energy partitioning within plasmas used to either produce or modify DLC films is not well understood. The present work focuses on investigating the fundamental chemistry of hydrocarbon plasmas used in DLC film processing as a means of understanding and ultimately controlling film fabrication. Here, we present a more holistic assessment of PECVD system used to create DLC films, including analysis of the gas-phase as well as the resulting materials. This comprehensive evaluation utilizing optical spectroscopy techniques and surface analysis tools (e.g., profilometry, contact angle goniometry, and Fourier transform infrared spectroscopy) is part of a larger effort to elucidate fundamental physical and chemical information on plasma processes that control deposition. For example, developing an understanding of energy partitioning within these plasma systems is a central component of this work as we have employed optical emission spectroscopy and broadband absorption spectroscopy to determine rotational and vibrational temperatures ($T_r$and T_v, respectively) of the CH radical in a variety of hydrocarbon precursor plasma systems. In CH_4 plasmas, T_v(CH) ranges from ~3000 to ~5000 K under most plasma conditions, whereas T_r generally reaches values ranging from 1000-2000 K. Both values appear to be correlated with system pressure and applied rf power. These results will also be presented in relationship to the properties of the deposited films. More importantly, data such as these provide valuable insight regarding possible mechanistic details in hydrocarbon plasmas linked to DLC film fabrication and help to unravel these complex systems with and without the presence of a substrate.

3:20pm **PS+TF-WeA4 ULK Film Dielectric Constant Restoration through Enhanced Organic Plasma Treatment**, ***Zhiguo Sun***, *J. Shu, P. Mennell, Q. Yuan, A. Madan, S. Molis, J. Mody, Y. Zhang, J. Shepard Jr,* GLOBALFOUNDRIES

Ultra low k (ULK) films has been successfully integrated into Back End of Line(BEOL) interconnect to maintain a lower RC delay to take advantage of transistor continuous scaling, and to keep power consumption at a low level. However, due to its intrinsic composition and porosity, ULK films are susceptible to damage during the following process, especially patterning process and wet process such as wet clean and CMP. It is desirable to restore the dielectric constant to its original number to get full benefit if low k value. In this study, We will report a novel plasma treatment method being able to enhance the film resistance to plasma damage and repair the plasma damage. Through the detailed comparison between the pristine films,, damaged films and repaired films through analytical methods including Ellipsometry Porosimetry(EP) ,Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Hg-probe, we find the organic plasma treatment capable of restoring the surface porosity, restore the lost methyl groups and restore the dielectric constant to its original value.

4:20pm **PS+TF-WeA7 Understanding of Low Temperature ALD of Silicon Nitride**, *H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK; *R.H.E.C. Bosch, T. Faraz, M. van Drunen, L.E. Cornelissen, M. Creatore,* ***Erwin Kessels,*** Eindhoven University of Technology, Netherlands

This contribution highlights insights into atomic layer deposition (ALD) of silicon nitride (SiN_x) and shows how considering these results in high material quality at low deposition temperatures. Thermal ALD processes generally require high temperatures for sufficient SiN_x quality and therefore plasma ALD has been studied extensively in the last few years. The model system discussed here consists of ALD processes using aminosilane precursors, such as $SiH_2(NH^tBu)_2$ (BTBAS) and $SiH_3N(^sBu)_2$ (DSBAS), and N_2 plasma as reactant.

Most plasma ALD processes for nitrides utilize NH_3 or H_2/N_2 plasmas, but for SiN_x it was found that the presence of H-containing species in the plasma strongly inhibits precursor adsorption.[1] DFT calculations demonstrated that groups with H on the surface have low reactivity with aminosilane precursors. Under-coordinated surfaces however, such as those obtained after N_2 plasma, have a much higher reactivity. To determine the nature of the surface, surface FT-IR studies were carried out. These indicated that the surface chemistry is rather complex as C and H species typically remain on the surface after the plasma step. Mass spectrometry showed that this can be related to reaction products that are created by the plasma step but which dissociate in the plasma and subsequently redeposit.[2] Shorter gas residence times reduce this redeposition effect and provide improved film properties (e.g., wet-etch rate, impurity content, and refractive index). The surface chemistry during the precursor step is relatively straightforward as gas-phase IR measurements and mass spectrometry measurements reveal that amino-groups from the precursor are released from the surface (e.g., in the form of H_2N^tBu). Note that not all the groups are released during the precursor step, as evidenced by the aforementioned redeposition effect.

Taking these aspects into account, high quality SiN_x layers were prepared by ALD at low temperatures. One particular example is that films prepared at 120 °C using BTBAS precursor and Ar/N_2 plasma were found to have excellent barrier properties against moisture.[3] Intrinsic water-vapor transmission rates in the range of 10^{-6} g/m^2/day were obtained for films as thin as 10 nm.[3] When DSBAS is used as precursor the redeposition effect appears to be reduced further, likely due to the fact this is a mono-aminosilane precursor. Precursor saturation, material quality and

conformality vary with precursor and plasma employed and these aspects will be discussed in the contribution .

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4:40pm **PS+TF-WeA8 Plasma Assisted Atomic Layer Deposition of SiC_xN_y Films with Methylamine as the Carbon Source**, ***Rafaiel Ovanesyan,*** *N. Leick, R.J. Gasvoda,* Colorado School of Mines*; K.M. Kelchner, D.M. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The introduction of 3-D device architectures in integrated circuits has created a need for atomic layer deposition (ALD) of highly conformal ultra-thin films. In particular, ALD of low-dielectric-constant, carbon-containing silicon nitride (SiC_xN_y) films at temperatures ≤400 °C is required. However, controlled incorporation of C atoms into SiN_x during ALD remains challenging.

In this work, we report the C incorporation mechanism during two plasma-enhanced SiC_xN_y ALD processes. The first ALD process consisted of three steps, Si_2Cl_6/thermal CH_3NH_2/N_2 plasma, while the second process consists of two steps, Si_2Cl_6/CH_3NH_2 plasma. In both ALD processes, we have determined the film composition, reactive sites, and adsorbed surface species using in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the growth per cycle (GPC) and refractive index were determined using in situ four-wavelength ellipsometry.

Our IR spectra show that in the first ALD process, the CH_3NH_2 thermally reacts with $–SiCl_x$ surface species created after the Si_2Cl_6 half-cycle to form -CH_x terminated surface amides. During the subsequent N_2 plasma half-cycle, in addition to nitridation of Si, a fraction of the surface CH_x groups were incorporated into the SiC_xN_y film as -N=C=N- species, which appear as a strong vibrational mode at ~2170 cm^{-1}. The composition of the SiN_x films in the two-step ALD process was very similar, with C incorporated primarily as -N=C=N- groups created during the CH_3NH_2 plasma half-cycle. We find that during the exposure of the film to Si_2Cl_6 following an CH_3NH_2 plasma half-cycle, surface carbodiimides (-N=C=NH) rearrange to nitriles (-NH-C≡N), while most of the surface is terminated with $–SiCl_x$ species. The subsequent CH_3NH_2 plasma half-cycle, shows that the-NH-C≡N species formed during the Si_2Cl_6 half-cycle are removed, and the N=C=NH surface species are restored along with $–NH_x$ groups. For the Si_2Cl_6/CH_3NH_2 plasma ALD process, SiN_x films grown at 400 °C show a carbon content of ~4 at.% as measured through Rutherford backscattering spectroscopy combined with hydrogen forward scattering. Transmission electron microscopy shows a conformality of >95% for the SiC_xN_y films. The GPC for both processes was ~0.9 Å, with a refractive index of 1.95 and 1.86 for the N_2 plasma and CH_3NH_2 plasma ALD processes, respectively.

5:00pm **PS+TF-WeA9 Plasma Enhanced Atomic Layer Deposition in the Semiconductor Industry**, ***Adrien LaVoie,*** Lam Research Corporation **INVITED**

Atomic layer deposition (ALD) has emerged as a key and enabling technology for <2X node fabrication methods in the modern semiconductor manufacturing toolbox. Today's applications range from front-end-of-line (FEOL) spacers and liners, isolation gapfill, FinFet conformal doping, multi-patterning layers, and through-Si-via (TSV) 3D liners. When considering ALD for HVM applications, the appropriate selection of platform and tool architecture is imperative with the goal of optimizing performance, reliability, cost, and throughput. In the first section, platform architecture features and requirements will be correlated to ALD market applications. In the second section, we focus on increasing throughput. Throughput demands have led to several hardware and process innovations including driving ALD towards operation in sub-saturation regimes. The greatest advantage of ALD is the self-limiting nature of the two half reactions which provides precise thickness control, extremely high film uniformity and conformality. However, the first half reaction of precursor adsorption requires saturation at longer times with diminishing growth per unit time when considering the dose saturation curve. The self-limiting nature is achieved at the expense of lower throughput and higher chemical consumption. An alternative is to perform "sub-saturated" processing in the sub-saturated regime. This presents a paradigm shift for ALD that permits conformal film deposition without satisfying saturated half reactions. Herein we demonstrate the modulation of dosing uniformity and conversion uniformity using various process parameters to achieve excellent wafer-to-wafer thickness control, within wafer non-uniformity and compositional uniformity. The utilization of the sub-saturation processing regime provides advantages in terms of throughput and chemical usage and has driven novel hardware designs.

5:40pm **PS+TF-WeA11 Substrate Biasing during Remote Plasma-ALD On Planar and 3D Substrates**, ***Tahsin Faraz,*** Eindhoven University of Technology, The Netherlands*; H.C.M. Knoops,* Oxford Instruments Plasma Technology, UK*; D.M. Hausmann, J. Henri,* Lam Research Corporation*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Ion-surface interactions during plasma-enhanced atomic layer deposition (PEALD) can influence the physical and chemical properties of the growing material. The limit to which ion-surface interactions can influence the deposition process depends on the energy and flux of the ions which are governed, in principle, by various process parameters. In a low pressure, remote inductively-coupled-plasma (ICP) reactor (e.g., Oxford Instruments FlexAL) capable of producing a wide range of ion fluxes, the ion energy can be controlled independently of the ion flux if equipped with substrate biasing. Previously, our group demonstrated that the material properties of thin films deposited on planar substrates using remote plasma-ALD can be tailored by controlling the energy of the impinging ions through substrate biasing.[1]

In this contribution, we will investigate the role of the ion energy via substrate biasing during remote plasma-ALD on both planar and 3D topologies. An upgrade to enable substrate biasing (up to 100 W, 13.56 MHz RF power, -500 V resulting DC bias) has been implemented in the FlexAL system in our laboratory. PEALD processes for SiN_x, a material used as gate spacers and hard masks during CMOS fabrication, were developed using aminosilane precursors and N_2 plasma.[2] The processes were modified by incorporating a tunable RF bias signal on the substrate table during the N_2 plasma exposure step which enabled control over the energy of the nitrogen ions impinging on the growing film. SiN_x films were simultaneously deposited on planar Si wafers and 3D trench nanostructures (AR ~ 4.5 : 1) using bias powers upto 10 W (~ -65 V resulting DC bias). The planar films deposited with biasing typically exhibited lower refractive indices and densities (~ 1.71 and 2.75 g/cm^3 respectively for -65V) compared to those deposited without biasing (~ 1.93, 3.13 g/cm^3). A 30s dilute HF etch treatment was performed on the films deposited on 3D trench nanostructures. Horizontal SiN_x film regions located at the top and bottom surfaces of the trench exhibited very high wet etch rates (WER) and were completely removed after the etch. However, vertical SiN_x film regions exhibited very low WERs (~ 3 nm/min) and remained selectively at the trench sidewalls post-etch. It will be discussed that the results observed could hold potential applications in multiple patterning and area-selective processing techniques, relevant for the fabrication of state-of-the-art FinFETs and next-generation "gate-all-around" FETs.

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6:00pm **PS+TF-WeA12 A Novel ABC-type ALD Process for Cobalt using $CoCp_2$ and N_2 and H_2 Plasmas**, ***Martijn Vos,*** *N.F.W. Thissen, A.J. Mackus, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

Cobalt is a transition metal which is receiving much interest, among others due to its ferromagnetic properties. One of the promising applications is in multilayers and alloys of Co/Pt, which are used in nonvolatile memory devices such as magnetic random-access memory (MRAM). For many of the applications of Co the key strengths of atomic layer deposition (ALD), i.e. conformality and ultimate thickness control, can be very beneficial. In previous work, the ALD processes using cobaltocene ($CoCp_2$) and NH_3 or N_2/H_2 plasma showed a decent growth-per-cycle (GPC) and good material properties, including a low resistivity.[1,2] It was found that the best material properties were obtained for a N_2/H_2 mixing ratio of ~0.33, corresponding to the highest production of NH_3 in the plasma. This result suggests that NH_3 is necessary for obtaining high purity Co films.

In this contribution we address ALD of Co films using $CoCp_2$ and subsequent N_2 and $HH_2HHfdfd$ H_2 plasmas. By comparing this ABC process to the AB process with a combined N_2/H_2 plasma the role of NH_3 can be further investigated. Moreover the ABC process offers additional flexibility over the AB process, such as different powers and pressures during the subsequent plasma steps. Films were deposited on different substrates, including Si, SiO_2 and Pt, at temperatures from 100 to 300°C yielding a GPC between 0.2 and 0.4 Å. It will be shown that despite the absence of NH_3 in the plasma, the ABC process can be used to deposit high-purity films of Co on ALD Pt films, with contamination levels as low as 1 at.%, as measured by X-ray photoelectron spectroscopy (XPS). On the other hand, considerable

amounts of C, O and N contamination (2-10 at.%) in Co films deposited on Si and SiO_2 suggest that NH_3 is a prerequisite for high purity films on these substrates. This difference between deposition on Pt and Si/SiO_2 is likely due to the catalytic activity of the Pt, causing the reduction or 'cleaning' of the deposited Co. In addition the fabrication of Co/Pt multilayers using ALD will be discussed.

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Plasma Science and Technology
Room 104C - Session PS-WeA

Atomic Layer Etching and Low Damage Processing

Moderator: Eric Joseph, IBM Research Division, T.J. Watson Research Center

2:20pm **PS-WeA1 Plasma-Based Removal of Native Oxide Layers on Si and SiGe Substrates While Minimizing Surface Residues***, D. Metzler,* ***Chen Li,*** University of Maryland, College Park*; C.S. Lai, E.A. Hudson,* Lam Research Corporation*; G.S. Oehrlein,* University of Maryland, College Park

The evaluation of a plasma-based native oxide surface cleaning process for Si and SiGe substrates is described. Objectives include removal of the native oxide while minimizing substrate damage and surface residues. This work is based on recent advances in atomic layer etching (ALE) of SiO_2[1]. To achieve controlled etching of SiO_2 at the Ångstrom level a cyclic approach consisting of a deposition step and etch step was initially employed. The deposition step deposits fluorocarbon (FC) films up to 10 Å thick on the surface. Subsequent low energy Ar^+ ion bombardment during the etch step induces mixing of the FC film with the substrate and removal of the FC film together with the mixed, reacted substrate material. Oxide layer thicknesses were measured using *in situ* ellipsometry and surface chemistry was analyzed by X-ray photoelectron spectroscopy. The cyclic ALE approach did not remove native oxide from a Si substrate at the level required. A modified process was evaluated which used continuously biased Ar plasma with periodic CF_4 injection. By eliminating a dedicated FC film deposition step, optimizing process times and ion energies, significant O removal from the Si surface was achieved, while leaving residual C. An additional H_2/Ar plasma exposure performed at higher pressure and minimizing ion bombardment successfully removed residual C and F originating from the surface cleaning process. The combined treatment reduced O and C levels to about half compared to as received Si surfaces but removed ≈37 Å of Si. Similar to Si substrates, SiGe substrate oxide removal was seen upon applying this cleaning process, while the H_2/Ar post treatment subsequently removed F and C-related species. O and C levels are reduced to ≈70% after the combined treatment while ≈55 Å of SiGe are removed. In addition, the surface is Ge richer after the cleaning process compared to SiGe surfaces as received. This feasibility study of Ar/FC based native oxide cleaning approaches for Si and SiGe substrates shows the potential to reduce O levels but at the cost of substantial substrate material loss and introducing low levels of C and F.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (CBET-1134273) and Lam Research Foundation.

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2:40pm **PS-WeA2 Electrical Characterization of SiN Modified by Hydrogen and Helium Plasma for New Atomic Layer Etching Processes***, Florentin Chambettaz, L. Vallier, O. Joubert,* Univ. Grenoble Alpes, France

As downscaling pace the microelectronic industry, current plasma etching processes show their limits. Actually for critical dimension smaller than 10 nm, atomic precision has to be reached. In this study, we are characterizing an Atomic Layer Etching (ALE) process by focusing on the induced damages related to the chemical and physical interaction(s) with hydrogen and helium plasmas. Hydrogen plasmas have been used for years in the microelectronic industry and studied in the fields of deposition (PECVD, Plasma Enhanced Chemical Vapor Deposition), surface processing (surface passivation, hydrogenation) [1] and plasma etching. However the mechanisms related to these processes are not fully understood yet mainly because hydrogen is an element with peculiar characteristics such as its low mass and electronegativity. Helium plasmas have been also used for many years in the microelectronics industry, mainly as an additives gas thanks to its low chemical reactivity and low mass. In order to modify the surface of ultrathin layers without damaging the materials, a very low ion bombardment is required (conditions similar to those obtained in a pulsed ICP reactor [2]). At the same time, dense plasmas are required to obtain satisfying etch rates when several nanometers have to be etched away. In this study we focus on plasma etching of silicon nitride by hydrogen and Helium plasma exposure in a commercially available 300 mm reactor, in order to develop an ALE process for spacer etching of future transistors [3]. Several process conditions are achieved with different ion energies and ion densities, on thin silicon nitride blanket samples. The quantity and the position in the silicon nitride of generated traps are studied with an electrical characterization. The effect of those plasma process condition on the silicon nitride etch rate will be discussed.

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3:00pm **PS-WeA3 Electron Beam Generated Plasmas Produced in Fluorine-Containing Gases***, David Boris, G.M. Petrov, Tz.B. Petrova, S.C. Hernandez, S.G. Walton,* Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma density (>10^{10} cm^{-3}), and very low electron temperatures (<1 eV) making them well-suited for next generation processing techniques where high fluxes of low energy ions are desirable. In addition, both modeling and optical emission spectroscopy indicate relatively low concentrations of radicals compared to discharges. In this work, we focus on the characteristics these plasmas in fluorine-containing chemistries (SF_6, C_xF_y, etc.), due to their relevance to industrial etching applications. We discuss the electron density and temperature, electronegativity, excited F* atom emission, as well as ion flux and energy at adjacent surfaces for plasmas produced in Ar/SF_6 Ar/F_2 and Ar/CF_4 mixtures, with particular attention paid to the influence of reactive gas concentration. These parameters are measured using Langmuir probes, optical emission spectroscopy, and energy-resolved mass spectrometry. The results are then compared with a one-dimensional, steady-state hydrodynamic model developed for electron beam generated plasmas produced in low pressure Ar-SF_6 mixtures.

3:20pm **PS-WeA4 Plasma-Enhanced Germanium Atomic Layer Etching (ALE)***, Wenbing Yang, S. Tan, K. Kanarik, R. Arghavani, T.B. Lill, Y. Pan,* Lam Research Corp.

Atomic layer etching (ALE) has been studied in the laboratory for more than 25 years and is being driven today by the semiconductor industry [1]. The case study ALE system is silicon ALE etched with alternating chlorine dosing and argon ion bombardment. Besides silicon, over 20 other materials have been reported with ALE including oxides, III-V compounds, and metals. Germanium, due to its superior hole mobility, is a prime candidate to replace silicon channel for use in future semiconductor devices. Two previous studies reported on germanium ALE in 1997. In the first study, Ikeda et al reported isotropic ALE of Ge by removing the chlorinated layer thermally [2]. In the second study, Sugiyama et al reported directional ALE of Ge by removing the chlorinated layer using argon ions [3]. In both reports, the chlorine was delivered thermally as a gas, without the use of plasma. Here we report on plasma-enhanced, directional Ge ALE. We will show results on both Ge blanket and patterned wafers and compare the behavior to the silicon case study.

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4:20pm **PS-WeA7 Damage Monitoring of GaN Film for Material Processing***, Daisuke Ogawa, Y. Banno, Y. Nakano, K. Nakamura,* Chubu University, Japan **INVITED**

Gallium nitride (GaN) is one of the candidate materials to realize miniaturized high power devices due to the wide band gap. The miniaturization of individual power devices, such as small inverters, are necessary to increase the electrical capacity, in particular, in upcoming electric vehicle era. In the last several decades, low-temperature plasma plays a role to speed computers up by fabrication. And now, the plasma is about to be applied to miniaturize high power devices. The advantage of the plasma processing is that a lot of semiconductor industries already have their own manufacture lines with the plenty of their processing

experiences. However, it is also well known that plasma can create undesired change on the processing devices. This is called plasma induced damage (PID), which is created by ions, radicals, radiations, dusts etc. GaN cannot be the exception of the damage creation so that better understanding of damage developments is important to increase manufacture productivity.

We have been analyzing the evolution of GaN condition during plasma processing to clarify the damage creation mechanism. In-situ monitoring is a key diagnostic to understand the mechanism so that we have mainly utilized photoluminescence (PL) from the GaN that is exposed in processing plasma. The PL gives us the information of the volume-averaged damages from the surface to approximately 45 nm depth. The depth range is important because the change in the range affects the device performance when fabricated. The PL also gives us the indication of the optically-emissive intermediate states that are mostly caused by impurities and crystal defects in GaN. In particular, it is possible to know what kind of damage a specific plasma creates by observing a specific wavelength range of the PL, such as near-band-edge (NBE), blue (BL) and yellow luminescence (BL) range.

In this presentation, we will summarize our damage analysis on GaN that is exposed in processing (etching) plasma. Understanding of damage creation mechanism from the plasma is not trivial because plasma creates the surface damage in addition to the temperature increase due to the ion bombardments. The temperature can assist physical deformation of GaN and chemical reactions on the surface. This means that the isolation between the damage creation and the temperature rise by the plasma might be a good idea to understand the mechanism. Interestingly, our former PL measurements showed that cooling GaN kept PL better than non-cooling GaN even when exposing argon plasma.

5:00pm **PS-WeA9 Neutral Beam Etching of Germanium Microstructure for Ge Fin-FET Devices**, *E.T. Lee,* ***Shuichi Noda,*** Tohoku University, Japan*; W. Mizubayashi,* AIST*; K. Endo,* AiST*; S. Samukawa,* Tohoku University, Japan

Germanium Fin-FET has becoming a promising candidates for highly scaled CMOS FETs to solve the limitation of device scaling of Si CMOS FET due to large carrier mobility of Ge itself. However, it seems that the etching mechanisms of Ge and optimization of etching method have not investigated deeply in spite of its importance forming basic channel structures in FET devices. Since we have already succeeded to apply a neutral beam etching (NBE) method to damage-free Si Fin-FET fabrication process and shown excellent device performances[1)], much more advantages in the low-damage NBE can be expected for Ge fin etching because thermal annealing is difficult due to a heat resisting property of Ge.

The NBE characteristics of Ge Fin were evaluated using pure Cl_2 gas chemistry which is the same for the Si Fin etching and compared results each other. The NBE system consists of an inductive coupled plasma (ICP) source and a carbon aperture plate where energetic negative ions are effectively converted to the neutral beam utilizing a pulse time modulated plasma. Ge Fin structure were etched with TEOS-CVD SiO_2 hard masks which were patterned by an EB lithography and a conventional ICP RIE. The sample substrate was set on the cooled stage at -15°C. The Ge profile was optimized by adjusting the beam energy which was controlled by changing the RF bias power to the carbon aperture.

The Ge Fin was etched at the etch rate of more than three times larger than Si. However, the large bottom tails were observed with different profile from the Si Fin structure. The etch rate difference can be explained due to the different etch yield and chlorination density on the surfaces[2)]. The large bottom tails of Ge Fin structure are considered to be caused by lower evaporation pressure of $GeCl_4$ than that of $SiCl_4$. The profile optimization was made by controlling RF bias power on the aperture plate. The bottom tail was reduced with increasing the bias power. The side-etching under the SiO_2 hard mask hardly increased during long over etch period. Conversely, the etch rate of Ge was almost constant regardless of the RF bias power. This results indicate that the etching reaction is limited by Cl supply, which chlorinates adsorption site on the Ge surface. The lateral etching is limited because the Cl radical density is low and the samples are cooled down to -15°C. The bottom tails seemed to be reduced in according to beam divergence narrowing. High magnification TEM images showed extremely smooth side wall surface in the substantially atomic revel.

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5:20pm **PS-WeA10 Selective Trimming of Surface Oxygenated Groups through Vacuum Ultraviolet Light Irradiation in an Evacuated Environment**, ***Ahmed Soliman,*** *T. Utsunomiya, T. Ichii,* Kyoto University, Japan*; H. Sugimura,* Kyoto University, Japan

Vacuum ultraviolet (VUV) light of 172 nm is widely used for modifying the surfaces of polymers and self-assembled monolayers (SAMs) to be applicable in microfluidics, lithography and microelectromechanical systems (MEMS) devices. The influences of VUV light on the surface modifications are dependent on the irradiation environment. In an atmospheric environment, the VUV light generates active oxygen species (O), which can functionalize and etch the organics at the irradiated surface.[1] While in high vacuum condition (HV), the rate of oxidation process at the VUV-irradiated surface decreased,[2] and other photochemical reactions, such as photo-cleavage can proceed apparently.

In this work, we examined the influence of HV-VUV treatment on the surface oxygenated groups of SAMs. We used VUV/(O)-modified hexadecyl (HD-) SAMs in this study, because of their highly-dense and well-defined structure. Furthermore, these modified-SAMs were homogenously terminated with different oxygenated groups.[1] These modified-SAMs were HV-VUV irradiated for different periods. The changes of the chemical constituents after HV-VUV treatment were characterized by X-ray photoelectron spectroscopy (XPS) and chemical derivatization using different fluorinated reagents.

After VUV/(O) treatment, the XPS results showed that the oxygenated groups at the surface of SAM contained both derivatizable (such as OH, CHO and COOH) and nonderivatizable (C-O-C, C-CO-C and C-COO-C) groups.[1] The HV-VUV affected the surface components; the decrease of COO and C-O moieties, while the slight increase of C=O moieties. The C-C components were slightly influenced by the HV-VUV irradiation. Considering the changes of the chemical constituents, wettability and morphology, the routes and mechanisms of the chemical conversions at the HV-VUV irradiated surface were discussed.

We concluded that the HV-VUV treatment to the surface oxygenated groups could only dissociate the components containing C-O bonds without significant influence on the C-C skeleton. The HV-VUV can be considered as a selective-trimming modification technique with less degradation, as the components containing C-O bonds were only dissociated.

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5:40pm **PS-WeA11 Transistor Performance Improvement Through Low-Damage Plasma-Enhanced ALD Metal Gates**, ***Christopher Brennan,*** *C. Neumann, S. Vitale,* MIT Lincoln Laboratory

Metal gate materials have now replaced polysilicon gates for advanced silicon CMOS fabrication of both planar silicon MOSFETs and FinFETs. However, plasma processes employed for metal gate deposition can cause significantly more damage to the gate dielectric material than with traditional chemical vapor deposition polysilicon gates, resulting in reduced device performance and reliability. Titanium nitride (TiN) is one such metal gate material, possessing both thermal stability and compatibility with gate dielectric materials. Additionally, the workfunction of TiN can be tuned to make mid-gap metal gates for undoped-body fully depleted silicon-on-insulator (FDSOI) transistors for subthreshold, ultra-low power operation. Gate dielectric quality remains critical for advanced device fabrication, especially for these low power, low leakage devices.

This work compares plasma-induced gate oxide damage by two different metal gate deposition processes: magnetron sputtering and plasma-enhanced atomic-layer-deposition (PE-ALD). FDSOI transistors fabricated with either gate deposition process showed similar electrostatic performance, with good short channel performance including subthreshold swing, DIBL, and V_t roll-off. However, gate dielectric quality metrics were significantly better when PE-ALD TiN was used compared to plasma sputtered TiN. CV measurements exhibited stretching of the curves and increased hysteresis with sputtered TiN compared to PE-ALD TiN, indicative of a higher density of interface states in the former case. In addition, gate leakage was 1200x higher for the plasma sputtered TiN devices, which is consistent with a high density of defects in the gate oxide leading to trap-assisted tunneling. Finally, transistors fabricated with both methods show that those fabricated with PE-ALD TiN demonstrate a significantly lower gate oxide failure probability.

Taken together, the electrical results suggest that plasma sputtering damages the gate dielectric through energetic ion and vacuum ultra-violet

(VUV) photon bombardment which breaks Si-O bonds and leaves defect states. In addition to higher leakage, these defect states can lead to device reliability issues and high early failure rates. Alternatively, inductively coupled plasma PE-ALD produces a much lower energetic ion and VUV flux at the wafer surface, resulting in markedly less damage. Instead of damaging the gate oxide, PE-ALD initially deposits a sub-nm TiOCN film which may serve as a passivating layer. This layer does not seem to induce any undesirable device characteristics except for a slight increase in EOT.

6:00pm **PS-WeA12 *In situ* Optical Diagnostics during Atomic Layer Etching of SiO_2 using Alternating Cycles of C_4F_8 and Ar Plasma**, *N. Leick,* ***Ryan Gasvoda,*** Colorado School of Mines*; A. van de Steeg,* Eindhoven University of Technology, Netherlands*; R.A. Ovanesyan,* Colorado School of Mines*; R. Bhowmick, E.A. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

Due to the continuous shrinking of semiconductor devices combined with the 3D architecture, the demands on dry etching processes have become increasingly stringent. Therefore, the development of more precise etching methods is necessary, and atomic layer etching (ALEt) is a promising technique to enable atomic-level thickness control, directional etching and material selectivity. Recently, ALEt of SiO_2 has been extensively studied, using a cyclic process that involves plasma deposition of a fluorocarbon (CF_x) layer, followed by an Ar plasma exposure to activate the fluorine for etching.

In this work, SiO_2 was etched using an ALEt process based on an octafluorocyclobutane (C_4F_8) plasma to deposit the CF_x layer and an Ar plasma for the removal of the material. In each ALEt half-cycle, *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry were simultaneously used to study the film composition and the change in film thickness, respectively. From these measurements, it was possible to conclude that under the C_4F_8 plasma conditions used, the CF_x layer can be deposited at a growth rate of ~1.65 Å/s, while minimizing the SiO_2 removal to negligible amounts. At the end of the CF_x deposition step, the predominant IR feature was centered at 1220 cm^{-1}, and can be attributed to CF_x (x=1,2,3), while some surface Si-C, Si-F and C-O can also be observed, suggesting the formation of an intermixed SiO_2/CF_x layer. In line with this result, the IR from the first 10 s of Ar plasma clearly shows the instantaneous removal of SiO_2. This removal continues for the 60 s of Ar plasma exposure, and ellipsometry enables us to distinguish between two etch regimes. The first regime has a high etch rate, ~0.5 Å/s, indicating a high F concentration in the intermixed SiO_2/CF_x layer. As the film etching proceeds, the intermixed layer becomes F-deficient which slows down etching, until finally the SiO_2 removal is dominated by inefficient Ar^+ sputtering. From these results, SiO_2/CF_x intermixing seems to be the dominant etching mechanism in this ALEt process.

In addition to the instantaneous removal of SiO_2, an increase in the CF_x signal was initially detected in the IR during the first 10 s of the Ar plasma exposure. Because at the end of the 60 s Ar plasma step no net incorporation of CF_x can be observed, we propose that CF_x is initially redeposited from the reactor surfaces and participates in the etching process. This redeposition increases the etch rate during the Ar plasma cycle by providing additional amounts of F from the gas phase, but also undesirably increases the etch rate with increasing ALEt cycles.

Plasma Science and Technology
Room 104C - Session PS1-ThM

Modeling of Plasmas and Plasma-Surface Interactions

Moderator: Sumit Agarwal, Colorado School of Mines

8:00am **PS1-ThM1 The role of the Singlet Metastables and Energy-dependent Secondary Electron Emission Yields in Capacitively Coupled Oxygen Discharges**, ***Jon Gudmundsson***, *H. Hannesdottir,* University of Iceland

We explore the effects of including the singlet metastable molecules $O_2(a^1\Delta_g)$ and $O_2(b^1\Delta_g^+)$ in the discharge model of a capacitively coupled rf driven oxygen discharge. We furthermore examine the addition of energy-dependent secondary electron emission yields from the electrodes to the discharge model. The one-dimensional object-oriented particle-in-cell Monte Carlo collision code oopd1 is used for this purpose [1], with the oxygen discharge model considering the species $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, $O(^3P)$, $O(^1D)$, O_2^+, O^+, O^-, and electrons. The effects on particle density profiles, the electron heating rate profile, the electron energy probability function and the sheath width are explored including and excluding the metastable oxygen molecules and secondary electron emission. We have demonstrated that adding the metastable $O_2(a^1\Delta_g)$ to the discharge model changes the electron heating from having contributions from both bulk and sheath heating to being dominated by sheath heating for pressures above 50 mTorr [2,3]. However, at a low pressure (10 mTorr), Ohmic heating in the bulk plasma (the electronegative core) dominates, and detachment by $O_2(a^1\Delta_g)$, has only a small influence on the heating process. Thus at low pressure, the electron energy probability function (EEPF) is convex and as the pressure is increased the number of low energy electrons increases and the number of higher energy electrons (>10 eV) decreases, and the EEPF develops a concave shape or becomes bi-Maxwellian [3]. We find that including the metastable $O_2(b^1\Sigma_g^+)$ further decreases the Ohmic heating and the effective electron temperature in the bulk region. The effective electron temperature in the electronegative core is found to be less than 1 eV in the pressure range 50 - 200 mTorr which agrees with recent experimental findings. Furthermore, we find that including an energy-dependent secondary electron emission yield for O_2^+-ions has a significant influence on the discharge properties, including decreased sheath width.

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8:20am **PS1-ThM2 A Computational Model for Magnetron Sputtering Devices using VSim**, ***James McGugan***, *C.D. Zhou,* Tech-X Corp.*; J.D. Smith,* Tech-X UK Ltd.*; C.M. Roark, A.Y. Pankin, P.H. Stoltz,* Tech-X Corp.

A 2D, axisymmetric model for a cylindrical magnetron is presented. The model is PIC based and performed in the software tool, VSim for Plasma Discharges. The effects of an external feedback circuit are investigated and an IV curve for the device is presented. The sputtering rate and erosion profile are obtained, and the erosion profile is input as an iterative geometry modification. The effects of this non-planar surface are calculated using a second-order cut-cell algorithm within the PIC algorithm. The modifications of the non-planar surface on the sputtering rate and yield are presented. Finally, the results are used to quantitatively predict device performance, longevity, and the atomic layer distribution of sputtered atoms on the target.

8:40am **PS1-ThM3 Three Dimensional Monte Carlo Simulation of Surface Charging on a Contact Hole during Pulsed Plasma Etching**, ***Yugo Osano***, *Y. Higuchi, Y. Nishizawa,* Samsung R&D Institute Japan*; M.H. Cha,* Samsung Electronics, Republic of Korea*; H. Kubotera,* Samsung R&D Institute Japan*; K.H. Lee,* Samsung Electronics, Republic of Korea

Three-dimensional (3D) simulation model has been developed to analyze the surface charging on a contact hole during plasma etching process, with emphasis placed on surface charging mitigated by employing pulse-time-modulated (TM) plasma. Surface charging and its influence on the trajectories of ions and electron are investigated with Monte Carlo (MC) procedure in level-set represented 3D-polygon geometries under uniform square lattice. The distribution of steady state surface charging is achieved by recursive calculation of charge accumulation from the ion/electron transport under the self-consistent electric field, and electric field is calculated by solving Poisson's equation for the accumulated charge. For the plasma description, time averaged ion/electron flux is used for continuous wave (CW) plasma, and the TM plasma is modeled by alternating two different sets of fluxes and incident energies of ions and electrons which corresponds to pulse-on and pulse-off states. The incident energy of electrons is set to be significantly lower in pulse-off state than in pulse-on state, to simulate decreased electron temperature during pulse-off. Calculations are performed for a silicon oxide contact hole with mask, where the surface geometry is shaped in an inversed truncated circular cone of aspect ratio ~10. Numerical results reproduced accumulation of surface charging showing distinct difference between CW and TM plasma. In a CW condition, surface charging is simply accumulated until the fluxes of electrons and ions become locally equivalent owing to their deflection by local electric field. Meanwhile, the distribution of surface charging varies at all time in a TM condition and exhibits significant contrast to CW (including sign of charging) upon TM plasma conditions such as duty ratio, frequency, etc. In accordance with charging distribution, the potential distribution is also significantly different between CW and TM plasma. The potential increases deeper in the contact hole with its maximum shown near at the bottom of the hole in a CW condition, whereas it shows fluctuating distribution in a TM condition.

9:00am **PS1-ThM4 Characteristics of Capacitively Coupled Plasmas Excited by Tailored Voltage Waveforms**, ***Ankur Agarwal***, *S. Rauf, K.S. Collins,* Applied Materials Inc.

Critical scaling limitations in microelectronics fabrication are increasingly driving the transition to 3D solutions such as multi-gate MOSFETs and 3D NAND structures. These structures create significant challenges for dielectric and conductor etching, especially given the high aspect ratio (HAR) of the features. Etching of HAR features require careful balance of the reactive species (ions and radicals) flux and ion energies else the via-like features may physically twist/turn due to the stochastic nature of fluxes entering the feature as the size of the opening shrinks or the critical dimension varies significantly along the depth of the HAR feature.[1] Capacitively coupled plasma (CCP) sources, commonly used for dielectric etching, enable separate control over the fluxes of ion and radicals and ion energies by utilizing multiple frequencies. The high frequency source allows for generation of large plasma density while biasing the wafer at low frequency controls the energy of the ions. However, interference effects between the driving frequencies have been shown where in even the low frequency contributes to plasma density and thereby affects ionization dynamics.

Recently, techniques such as electrical asymmetry effect and non-sinusoidal voltage waveforms have been developed which purport to overcome the interference effect and thereby provide active separation of ionization level and ion energy distributions.[2,3] Much of this work has focused on either a geometrically symmetric system or for high pressure deposition processes. In this work, we investigate the plasma characteristics of CCPs driven by non-sinusoidal voltage waveforms in a geometrically asymmetric chamber as is typically utilized for plasma etching. Results will be discussed from a 2-dimensional plasma equipment model will be discussed for varying voltage waveforms which are generated using up to 5 harmonics similar to Bruneau et al.[3] Characterization of active species identity, fluxes and energies will be discussed for varying gas pressure in argon and fluorocarbon gas mixtures.

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9:20am **PS1-ThM5 Multi-zone Equilibrium of ICP Discharge for Plasma Processing. Mechanism of Plasma Heating**, ***Vladimir Nagorny***, Mattson Technology

ICP discharges and plasma sources are quite common in semiconductor plasma processing. Many

observations, plasma measurements and even simulations, including multiple species were published

through the years. However theoretical considerations were limited to a case when plasma

equilibrium can be characterized as global. In a real processing plasma this kind of equilibrium is

unstable. Here we analyze more real case when equilibrium consists of at least two areas - one is a

band-like area with self-sustaining plasma, where most of plasma generation occurs is linked on one

side to the induction coil and absorbs all the energy directly from the coil. On the other side

this band is linked to the second - plasma transfer area, which is fed by the energy and particles

escaping from the first area. The second area is also linked to surrounding walls. In a way, this

structure of ICP discharge reminds a glow discharge structure. The first - plasma generating area

functions similar to a cathode fall, and the plasma transfer area - similar to a positive column.

The number of plasma generating zones depends on the number of coils and construction of the coil,

and is usually more than one plasma generating zones are linked to a common plasma transfer zone.

Keywords - Plasma Processing, Inductively coupled plasma, ICP discharge, Plasma Sources

9:40am **PS1-ThM6 Characterization of Transients in Pulsed Capacitively Coupled Plasmas***, **Wei Tian**, A. Agarwal, S. Rauf, K.S. Collins,* Applied Materials Inc.

Plasma etching processes for microelectronics fabrication at future technological nodes are extremely challenging. The requirements regarding the uniformity (both etch rate and critical dimensions) and selectivity are also more stringent than ever. To meet these strict requirements, it is important to control the flux of ions and radicals to the substrate and energy of the ions incident on the substrate. In capacitively coupled plasmas, this control is typically achieved by varying the gas mixture, frequency, or pressure. Pulsing the plasma also enables one to modulate the electron energy distributions and the electron impact source functions of reactive species, which may be not otherwise possible using traditional methods.[1,2] Although pulsed capacitively coupled plasmas (CCPs) has been experimentally and computationally investigated before, there is little understanding of the transients during a given pulse. Of particular interest is the characterization during transition from after-glow to active-glow and vice-versa when the plasma impedance varies rapidly.

In this work, we will discuss the transients in pulsed CCPs using results from a 2-dimensional plasma equipment model. The model is validated against experimental measurements for Ar/O2/CF4 mixtures.[3] Asymmetric ignition of the plasma is observed in some cases which can have significant consequences on time-averaged plasma uniformity. Depending on the operating conditions, oscillations in bulk plasma are also observed which last many rf cycles. These oscillations can be attributed to the negative ions bouncing between the rapidly expanding sheaths during early active-glow. The consequences of gas mixture, pulse duty cycle and pulse frequency on the plasma characteristics during the initial active-glow phase and after-glow phase will be assessed.

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11:00am **PS1-ThM10 Modeling and Simulation of Nonequilibrium Atmospheric Pressure Plasma Flows***, **Juan Trelles**,* University of Massachusetts Lowell **INVITED**

Atmospheric pressure plasmas are at the core of diverse technological applications, from materials processing and chemical synthesis, to waste treatment and environmental remediation. These plasmas display high collision frequencies among electrons and heavy-species (molecules, atoms, and ions). The interaction of atmospheric pressure plasmas with the processing media, such as a gas stream, produces significant deviations from the Local Thermodynamic Equilibrium (LTE) state, manifested by dissimilar velocity distributions between electrons and heavy-species, leading the plasma to a state of thermodynamic nonequilibrium (non-LTE or NLTE). Moreover, such interactions are characterized by large variations in flow properties and complex coupling among fluid flow, heat transfer, chemical kinetics, and electromagnetic phenomena. These characteristics impose severe challenges to numerical modeling and simulation approaches, which include resolution of multiscale features, multiphysics coupling, and robustness in the presence of large solution field gradients. An overview of the modeling and simulation of nonequilibrium plasma flows using the Variational Multiscale (VMS) Finite Element Method (FEM), one of the most robust, versatile, and widely used techniques for the numerical solution of multiphysics problems, is presented. The plasma is modeled as a compressible reactive electromagnetic fluid in chemical equilibrium and thermodynamic nonequilibrium. Material properties vary in a markedly nonlinear manner and by several orders of magnitude, which severely stresses the robustness required from the numerical methods. The VMS methodology treats the plasma flow model as a coupled system of transient-advective-diffusive-reactive transport equations, which naturally allows the extension of the approach to other plasma models. Simulation results of canonical and industrially-relevant atmospheric pressure nonequilibrium plasmas, namely the plasma flow in transferred and non-transferred arc plasma torches and the free-burning arc, demonstrate the effectiveness of the method. Particularly, the simulation approach is capable to capture the complex arc dynamics inside plasma torches, including the arc re-attachment process, as well as the spontaneous formation of self-organized anode patterns in the free-burning arc. The results indicate the suitability of the VMS-FEM for its application to other types of plasma flow models and the simulation of other plasma-related processes.

11:40am **PS1-ThM12 Multiscale Approach for Deep Silicon Etching Simulation under Bosch Process using SF_6 and C_4F_8 Plasma Chemistry***, **Guillaume Le Dain**, A. Rhallabi,* Institut des Matériaux Jean Rouxel – Université de Nantes, France*; M. Boufnichel, F. Roqueta,* ST Microelectronics, France

Deep silicon etching is now used in many semi-conductor devices such as high power devices, Micro-Electro-Mechanical-Systems (MEMS) and Systems In Package (SIP). The aim of deep silicon etching is to perform high aspect ratio profiles with a minimum of geometrical defects such as roughness and undercut. Bosch process is one of dry etching processes used for silicon deep etching. It is based on cyclic process consisting of alternating etching and deposition pulses. The optimization of this kind of etching processes for different applications requires a good understanding of the plasma surface interactions. Etching simulator can be considered as a complementary tool to improve the quality and the reliability of the silicon etch profile. In this context, we have developed a multi-scale approach to simulate the silicon etch profile evolution as a function of the operating conditions of Bosch process, performed in ICP reactor. Etching pulse is ensured by SF_6/Ar plasma mixture while the deposition pulse is ensured by C_4F_8 plasma.

Our silicon etching simulator is thus composed of three models:

- 0D plasma kinetic models of SF_6 and C_4F_8

- Sheath models of SF_6 and C_4F_8

- 2D Surface model

0D kinetic model is based on the solving of the mass balance equations of all neutral and ion species considered in the reaction scheme coupled to charge neutrality equation and power balance equation. The solving of the non linear equation system, until it reaches to steady state. This solving allows to calculate the fluxes of neutral and ion species as well as the electron density and temperature. Those information are introduced as input data in the sheath and etching models. The sheath model provides angular and energetic ion distribution functions which are required in the quantification of the ion sputtering on the local etched surface.

The surface model is the third model which is based on the cellular Monte-Carlo method to describe the plasma surface interactions in a probabilistic way for silicon etching through the mask. Atomic fluorine and positive ions produced during SF_6 plasma discharge are considered as the reactive species in the etching process steps while the C_xF_y radicals and positive ions are considered as the reactive species in the surface passivation steps.

The simulation results show the pressure variation which affects the etch profile especially the scalloping and the undercut effects. On the other hand the comparisons between the simulation and the experiment in terms of trenches aspect show a satisfactory agreement.

12:00pm **PS1-ThM13 Molecular Dynamics Simulation of Ni Etching by CO Plasmas***, **Akito Kumamoto**, N. Mauchamp, M. Isobe, K. Mizotani, H. Li, T. Ito, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

Magnetic random access memory (MRAM) is a nonvolatile storage device of high speed operation with low operating voltage. It has the potential to replace static random access memory (SRAM), dynamic access memory (DRAM), and flash memory if the MRAM integration becomes comparable

to that of DRAMs. One of the key challenges for high integration of memory cells in an MRAM device is to establish low-damage highly anisotropic etching technologies for magnetic thin films. Although Ar ion milling processes have been widely used to etch magnetic thin films for MRAM chip manufacturing, plasma etching based on chemically reactive gases such as CO/NH3 and CH3OH have been also studied as possible reactive ion etching (RIE) processes. In this study, we have used molecular dynamics (MD) simulations and ion beam experiments to understand etching mechanisms of magnetic thin films by chemically reactive plasmas. More specifically the current goal of this research is to develop classical interatomic reactive potential functions for MD simulation to emulate etching processes of magnetic thin films (Ni, Co, Fe, and CoFeB alloys) with high accuracy. In this study, we have used Ni as a sample film and developed Ni-C-O interatomic potential functions to examine self-sputtering and physical sputtering by energetic inert gas ions as well as oxidation and carbonization of Ni surfaces by incident O+, C+, and CO+ ions. The metal-metal interactions are modeled with embedded atom method (EAM). However, the existing EAM potentials for most metals do not reproduce their self-sputtering yields well and therefore require modification of the functions in the short range. The metal-oxygen or metal-carbon interaction model used in our MD simulation is based on bond-order potential functions or Stillinger-Weber type angle dependent three-body functions. The potential function model also includes coordination bonds to allow the possible formation of metal carbonyls such as Ni(CO)4. The parameters of these potential models have been optimized based on experimental data of sputtering yields as well as potential energy data obtained from first-principle quantum mechanical (QM) simulations. The MD simulation results for Ni etching based on the newly developed reactive potential functions are also compared with data obtained from ion beam experiments.

Plasma Science and Technology
Room 104B - Session PS2-ThM

Plasma Processing of Challenging Materials

Moderator: David Ruzic, University of Illinois at Urbana-Champaign

8:00am **PS2-ThM1 Epitaxy of Doped Diamond for Electronics and Energy Applications Using Microwave Plasma CVD**, ***Robert Nemanich***, *F.A. Koeck,* Arizona State University **INVITED**

Diamond has been considered as the ultimate power semiconductor because of its wide bandgap, high electron and hole mobilities, low dielectric constant and highest thermal conductivity. Recent availability of CVD diamond plates with defect densities less than 1E5 cm-2 has presented the opportunity to fabricate and characterize diamond devices. While p-type doping with boron has been known for a number of years, n-type doping during CVD growth has recently been achieved using phosphorus as the dopant. The early studies established that phosphorus can be incorporated for growth on (111) surfaces, but the incorporation is much less efficient for growth on (100) surfaces. This report describes microwave plasma CVD approaches for P-doping on both 100 and 111 surfaces while maintaining high quality epitaxy. For the (100) surfaces a pulsed growth approach is presented which results in a P-incorporation density greater than 1E18 cm-3. For growth on (111) surfaces incorporations rates approaching 1E20 cm-3 have been obtained. Using these growth approaches pin diodes have been prepared on both (111) and (100) substrates. Diodes on (100) surfaces with breakdown voltages greater than 600V have been prepared and characterized. These diodes show high forward current densities of greater than 100 A/cm2 at 5V. The diodes prepared on (111) substrates show a turn-on between 4 and 5 V indicating bipolar characteristics. An approach for fabricating pnp bipolar junction transistors is described. Simulation results indicate operation at high voltage and high power with a gain that could approach 100. The use of P-doped layers for thermionic emitters and thermionic energy conversion is also described. The P-doped diamond layers show a workfunction less than 0.8 eV which could enable a leap in thermionic energy conversion efficiency.

This research supported by ARPA-E through the SWITCHES program and by the Office of Naval Research.

8:40am **PS2-ThM3 Magnetic Degradation of Perpendicular CoFeB Film caused by Hydrogen Plasma**, ***Masaki Yamada***, Hitachi High-Technologies Corporation, Japan; *M. Satake,* Hitachi High-Technologies Corporation

The RIE etching of p-MTJ (Perpendicular Magnetic Tunnel Junction) device is one of big issues to realize the high density STT-MRAM (Spin Transfer Torque Magnetoresistive Random Access Memory). In the view point of high etching selectivity or corrosion-less, Ar/CH_3OH or CO/NH_3 is generally used in MTJ etching. On the other hand, according to recently report, the hydrogen plasma in etching gas may cause the electrical degradation [1]. In this study, we investigate the influence of hydrogen plasma on magnetic properties by using thin CoFeB blanket film.

The stacked film structure is Ta(t_{Ta}) / MgO (2.0nm) / CoFeB(t_{CoFeB}) / Ta(5nm) / substrate, which were deposited on Si substrate by UHV RF-sputtering apparatus. In this study, CoFeB film thickness t_{CoFeB} were varied from 1.0 nm to 2.0 nm. Then they were annealed at 300 degC for 1 hour with $\mu_0 H$ = 0.6 mT. After that, the hydrogen plasma was irradiated to the film for 5 min through Ta capping layer by using Inductively Coupled Plasma etcher. The magnetization of blanket CoFeB films were evaluated by using Vibration Sampling Magnetometer.

At first we evaluate the CoFeB film thickness dependence of magnetic anisotropy. Without plasma irradiation, the magnetization of CoFeB film shows a perfect perpendicular anisotropy at t_{CoFeB} = 1.2 nm and its coercivity $\mu_0 H_c$ is obtained as $\mu_0 H_c$ = 0.8 mT. On the other hand, when the hydrogen plasma is irradiated to stacked film, the coercivity decreases down to $\mu_0 H_c$ = 0.2 mT. And also its effective perpendicular anisotropy field $\mu_0 H_k$ also decreases from $\mu_0 H_k$ = 330 mT to $\mu_0 H_k$ = 220 mT with hydrogen plasma irradiation. In the case of t_{CoFeB} = 1.4 nm, the magnetization shows weak perpendicular anisotropy before plasma irradiation. In this situation, the magnetization drastically changes from the weak perpendicular to in-plane anisotropy by hydrogen plasma irradiation. These results imply that the interfacial perpendicular anisotropy energy decreases by hydrogen plasma irradiation. Next we evaluate capping layer thickness t_{Ta} dependence of magnetic anisotropy. In the case of t_{Ta} < 20 nm, the coercivity of CoFeB film increases with increasing Ta capping film thickness with hydrogen plasma irradiation. And it shows approximately constant value at t_{Ta} > 50 nm even with hydrogen plasma irradiation. This behavior is well described by the hydrogen plasma diffusion model in Ta capping layer, which is calculated by Monte Carlo simulation. From present study, we found that hydrogen plasma may attack to MgO layer chemically and it may deteriorate the perpendicular magnetization of CoFeB.

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9:00am **PS2-ThM4 Roughness and Selectivity Trade Off during Patterning using Next Generation Resist**, ***Vinayak Rastogi***, *A. Ranjan,* TEL Technology Center, America, LLC

Optical lithography has reached its physical limit and eventual capacity to extend validity of Moore's law. Augmentation of 193i with multiple patterning, Extreme Ultraviolet Lithography and Directed Self Assembly are viable contenders to enable scaling for future technology nodes. However each patterning technique comes with common challenges of 'high initial pattern roughness' and 'etch resistance', the correction/compensation of which becomes more critical as we work on smaller dimension features. Plasma Etch processes have the potential to improvise upon the incoming pattern roughness and improve LER/LWR downstream with enhanced selectivity to thinner resist for expediting sub 10nm technology development.

In this work we demonstrate the specific role of passivation control in the dual-frequency Capacitively Coupled Plasma (CCP) with thin (EUV) resist patterning as an example process to improve LER/LWR, resist selectivity and CD tunability for line/space patterns. We will draw the implicit trends between different passivation chemistry and their effectiveness for roughness improvement. The effect of relative C:F and C:H ratio in feed gas on CF_x and CH_x plasma species and in turn the evolution of pattern roughness is drawn. Data that evinces the role of plasma etch parameters impacting the key patterning metrics of CD, resist selectivity and LER/LWR will be presented.

9:20am **PS2-ThM5 Fabrication of Large Superhydrophobic Surfaces with Hierarchical Structures on Polymer Films – Influence of the Roughening and the Fluorination**, ***Jérôme Durret***, *N. Frolet, C. Gourgon,* CNRS - LTM, France

Superhydrophobic (SH) surfaces exhibit many useful characteristics for various industrial applications [1]. Many strategies have been put forward [2] on small surfaces including efficient plasma treatment [3]. It is of great

interest to create large and flexible SH surfaces, making polymer films a promising solution. In this work, a two-step method for producing SH large and flexible surfaces from hydrophobic or hydrophilic polymer film materials is described.

Hierarchically structured SH surfaces were fabricated using NIL for submicro scale structuration and plasma treatment for nanoscale structuration. Hydrophobic (FEP) and hydrophilic (PMMA) polymer film materials were used. The roughening of nanoimprinted films by plasma treatment with Ar/CF4 gas flow is reported in a capacitive coupled parallel reactor. Water contact angles (WCA) greater than 160° and contact angle hysteresis (CAH) less than 1° have been measured for a plasma treatment of only 10s. The effect of the input power (600 to 1800 W) has been investigated in terms of roughening and fluorine percentage (%F), see Fig. 1, and Fig. 2 for XPS spectra. This representation enables us to discriminate the influence of the roughness and %F. Indeed, from 800 W plasma treatment, and despite variations of the %F, the wettability remains unchanged due to a sufficient roughness. Fig. 3 shows corresponding SEM images. Additionally, Fig. 4 shows that during plasma treatment, PMMA becomes first hydrophobic as the fluorination increases (from 0 to 39%) and finally superhydrophobic with the increasing roughness.

A modification of the dot dimensions during the plasma treatment is observed as can be seen in Fig. 5. Moreover, fracture defects still remain when fabricating high aspect ratio patterns by NIL [4]. We propose to overpass this limitation by using NIL patterning only as a preliminary step to define the dot diameter. Then the desired height can be achieve by a plasma transfer. Promising results were obtained on rough dots, see Fig. 6.

In the prospect of an industrial application, all process were developed on large areas (50 in² or 320 cm²). Thus, large, flexible and transparent SH films were obtained. Finally, thanks to the combination of NIL and plasma transfer, these films may be used to fabricate high aspect ratio patterns.

This work has been partially supported by the Direction Générale de l'Armement (DGA) and the Renatech network.

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9:40am **PS2-ThM6 Chlorine-based Etching of InP Laser : Effect of Plasma Chemistry on Sidewall Roughness and Damages**, ***Guillaume Gay***, *E. Pargon, C. Petit-Etienne,* LTM - CEA/LETI, France*; M. Brihoum, S. Barnola,* CEA, LETI, MINATEC Campus, France*; S. Labau, S. Arnaud,* LTM - CEA/LETI, France

Development of photonic devices on silicon could open the path to the design of new components, mixing optoelectronics and microelectronics. However, indirect band of silicon makes an all-silicon photonic device impossible. An alternative is the hybrid integration which consists in building active laser emitters with III-V materials, and other components (waveguides, filters, photodetectors) with silicon-based materials. In this study, we will focus on the dry etching of Indium-Phosphide (InP) for laser emitter fabrication reported on 200mm silicon-on-insulator wafer by molecular bonding. The major challenges related to this integration are (i) high InP etch rates necessary for micrometric high lasers, (ii) high selectivity toward silicon oxide to preserve the underneath passive components, (iii) anisotropy and (iv) smooth and undamaged surfaces. Plasma etching experiments are carried out in an inductively coupled plasma reactor from applied materials equipped with a hot cathode. In order to achieve these objectives, two plasma chemistries were developed: $Cl_2/CH_4/Ar$ and Cl_2/N_2. They will be compared in terms of profile, roughness, surface chemical composition, and a particular attention will be paid on the chemical and physical damages induced on the pattern sidewalls. The pattern profiles are characterized by electron microscopies. The sidewalls roughness is measured by AFM using a homemade setup where the sample is tilted to allow the tip to scan the sidewalls. The sidewalls chemical composition and stoichiometry after etching is analyzed by EDX. In $Cl_2/CH_4/Ar$, the process performance is mainly driven by the CH_4 flow. The anisotropy is ensured by the redeposition of SiO_xC_y byproducts, coming from the SiO_2 wafer, on the InP sidewalls. A compromise has been found to ensure anisotropy and sufficient selectivity of InP over the SOI substrate. Sidewall roughness on InP patterns is very close to the one measured on the mask sidewalls before etching, thus proving that this etching process does not produce supplementary roughness. Concerning Cl_2/N_2 plasma, etching selectivity is high and leads to highly anisotropic profile. In that case, the sidewall passivation layer is formed by the preferential etching of indium by chlorine, leading to a phosphorus-rich layer. The counterpart is that this P-rich layer also forms on the open-area and is responsible for roughness formation. Afterwards, we will also consider different strategies to remove these passivation layers so as to obtain clean InP ribbons sidewalls suitable for laser emitter fabrication.

11:00am **PS2-ThM10 Using a Dielectric Barrier Discharge (DBD) Device to Produce Proton Exchange Membranes at Atmospheric Pressure for PEMFC Technology**, ***Joffrey Baneton***, *D. Merche,* Université Libre de Bruxelles, Belgium*; G. Caldarella, N. Job,* Université de Liège, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

The polymer electrolyte membrane is one of the most important components of proton exchange membrane fuel cells (PEMFC) because it transports the ions from one side of the cell to the other one while it prevents the passage of the electrons and then the offsetting of the accumulated charges at each electrode. It is also important for device structure and gas permeability considerations [1]. Over the years, several methods have been developed to replace conventional techniques that involve many steps and the use of solvents and expensive reagents. Some studies exhibit an interest for low-pressure plasma devices to produce sulfonated polystyrene membranes [2]. In this work, we propose an innovative approach using an atmospheric-pressure dielectric barrier discharge (DBD) with styrene as carbon matrix reagent and acid precursors (such as trifluoromethanesulfonic acid) to integrate proton exchange groups. Using this atmospheric plasma device allows to produce membranes in a 'one-step' process, avoiding solvents and vacuum constraints [3]. X-ray photoelectron spectroscopy (XPS) and infra-red reflection absorption spectroscopy (IRRAS) are used to determine the chemical composition of the membranes. Stylus profilometry and scanning electron microscopy (SEM) are applied to analyze their morphology. Electrochemical measurements are also performed to determine the membrane proton conductivity.

In the case of pure polystyrene films, it is shown that the plasma leads to the polymerization of the monomer without altering their chemical structure. Moreover, the optimization of the reactor geometry and the experimental variables such as the flow rate, the injected discharge power, the precursor temperature or the duty cycle (in the case of pulsed plasma) can lead to the formation of homogeneous and uncontaminated films. In the case of copolymerized membranes using an acid precursor, a high content of fragmented and distributed proton exchange groups can be observed on the XPS and IRRAS spectra.

This work was financially supported by the Walloon Region (HYLIFE project n°1410135, Energinsere program) and by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

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11:20am **PS2-ThM11 Laser-Enhanced Plasma Etching of Semiconductors and Metals**, ***Jason Peck***, *G.A. Panici, I.A. Shchelkanov, S. Hammouti, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Dry etch assisted by laser (DEAL) of silicon and copper via Ar/C4F8/O2, Ar/SF6, and Ar/CCl4 capacitively-coupled plasma was studied, with goals including form control for sub-22 nm features and uniformity for 450 mm wafer processes. The first phase of the study consisted of wavelength (1064, 532, 266 nm) investigation, variation of gas chemistry, and laser intensity ramping. Multiple lasers were employed to vary repetition rate, from CW, 100 Hz, or 100 kHz, as well as varied pulse width, 350 fs to 7 ns, to understand instantaneous laser power against gas dynamics timescales.

The second phase of the study explored multiple material candidates, focusing particularly on metal etch. The etch rate enhancements were determined in the case of Si and Cu etch. Etch activation in zero-etch recipes was achieved upon introduction of 532/266 nm wavelength in the case of silicon and 1064 nm in the case of copper. In particular, Cu etch was demonstrated at substrate temperatures (40-70°C) far below the required temperature to produce a volatile etch product. Scalability and the ease of incorporating this technique into industry processes will be discussed.

11:40am **PS2-ThM12 Highly Selective Isotropic Etching of Silicon in Preference to Germanium**, ***Christopher Ahles***, *A.C. Kummel,* University of California, San Diego

As CMOS technology is scaled down to <10nm, new MOSFET architectures are required in order to maintain control over the device. The optimal design for such a device is the gate-all-around (GAA) architecture. Whereas in previous CMOS generations the MOSFETs were planar structures, GAA structures require highly selective isotropic etching for device fabrication. Previous isotropic gas phase selective etching of silicon employed sulfur passivation of Ge which can dope silicon, corrode process equipment, and cause ion mobility in dielectrics. In this report a sulfur-free isotropic selective etch is reported which has essentially infinite Si/Ge etch rate ratio (ERR) using in a downstream plasma. The etch rates of Si and Ge were simultaneously measured in-situ using a reactor chamber equipped with dual quartz crystal microbalances (QCMs). The gold-coated quartz crystals were sputter-coated with Si and Ge. After in-situ removal of the surface oxides with a downstream NF3/H2 plasma, the Si and Ge films were dosed with gas from a downstream plasma of H2, CF4 and Ar. It was found that a high Si/Ge ERR can be obtained over a wide range of H2/CF4 gas flow ratios, QCM temperatures, chamber pressure and plasma power. For the optimal process window, there is an etch rate >1nm/min for Si and deposition of carbon onto Ge. The nature of the passivation layer is being investigated via XPS as well as isotopic labeling in conjuction with secondary ion mass spectrometry (SIMS) studies. It is hypothesized that the high selectivity occurs due to the occupied Ge d-orbitals backbonding with an unsaturated carbon ligand, such as a CF2 carbene. This backbonding promotes the polymerization of a carbonaceous film on the Ge surface and thereby passivates the Ge against etching. Since Si does not possess occupied d-orbitals it is unable to promote the polymerization of a passivation layer as efficiently as Ge.

12:00pm **PS2-ThM13 Thermodynamic Prediction and Experimental Verification of Etch Selectivity for EUV Mask Materials**, ***Luke Minardi***, *N.D. Altieri, E.L. Chen, J.P. Chang,* University of California Los Angeles

Extreme ultraviolet (EUV) lithography is a promising candidate to replace optical lithography and extend Moore's Law. EUV lithography requires reflective optics due to the strong absorption of EUV light by most materials. The exposed wafer area is defined by the absorbing and reflecting regions of the EUV mask. The absorber stack in the EUV mask consists of 2-10 nm TaON antireflective coating (ARC) and 50-60 nm TaN bulk absorber. The final EUV mask must have a ±1 nm absorber thickness uniformity and a mean-to-target critical dimension of 2.0 nm[1,2]. The etch process to pattern the EUV mask must be highly selective and anisotropic to meet the stringent requirements on mask dimension.

In this work, a generalized thermodynamic approach was used to screen viable etchants and predict selectivity. Gibbs energy minimization (GEM) was used to screen a library of halide containing etchants for efficacy on Ta-based compounds. Using GEM, Cl-based etchants indicated a high selectivity of Ta to Ta_2O_5. For example, at 350 K and 10^{-5} atm, 1 kmol of $Ta_{(s)}$ in the presence of 33 kmol of Cl_2 forms 1 kmol of $TaCl_{5(g)}$ while 0.5 kmol $Ta_2O_{5(s)}$ remains unreacted in 33 kmol of Cl_2. Volatility diagrams were constructed for the Cl_2-Ta and Cl_2-Ta_2O_5 systems to compare etch product volatility at specified Cl_2 pressure. For the Cl_2-Ta system at a chlorine pressure of $\log(P_{Cl2})$=-5 atm, it is predicted that $TaCl_{5(s)}$ is in equilibrium with $TaCl_{5(g)}$ at a partial pressure of $\log(P_{TaCl5})$=-6 atm. For the Cl_2-Ta_2O_5 system at a chlorine pressure of $\log(P_{Cl2})$=-5 atm, it is predicted that $Ta_2O_{5(s)}$ is in equilibrium with $TaCl_{5(g)}$ at a partial pressure of $\log(P_{TaCl5})$=-40 atm. Using GEM and volatility diagrams it was predicted the etch rate of $Ta_{(s)}$ >> $Ta_2O_{5(s)}$ in a Cl_2 environment. Selectivity predictions have been tested and verified experimentally through etch rate experiments using an inductively coupled plasma etcher. Experiments conducted at 250 W power, 10 mTorr, and 20 sccm Cl_2 determined selectivity to be 360 and 68 at bias powers of 0W and 10W, respectively. Although plasma processing is inherently non-equilibrium, thermodynamic prediction of product volatility is a powerful tool indicating trends in etch rate.

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Plasma Science and Technology
Room 104B - Session PS-ThA

Plasma Chemistry and Plasma Surface Interactions

Moderator: Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS-ThA1 Nonthermal Plasma Driven Power to Gas**, ***Tomohiro Nozaki,*** Tokyo Institute of Technology, Japan **INVITED**

Renewable energy is recognized as indispensable CO_2-free energy source in our future society and tremendous increase in renewable energy has been demanded worldwide. However, it is also well-known that energy generation and timing strongly fluctuate depending on the climate and geological conditions. Energy storage by secondary batteries and smart grid concept have been investigated extensively by now. More recently, power to gas (PtG) concept is highlighted. The key component of PtG is the electrochemical conversion of H_2O into H_2 and O_2 with renewable electricity, enabling direct conversion of electrical energy to chemical energy. Basic concept of PtG can be extended to the synthetic CH_4 production from CO_2 and renewable hydrogen for increased energy storagibility and transportability. The key strategy is that electrochemical H_2O conversion and conventional C1 chemistry, which utilizes thermal energy at various temperature range, is combined appropriately in order to maximize overall electrical to chemical conversion processes.

In this study, nonthermal plasma enhanced catalytic conversion of CH_4 and CO_2 into syngas (CO and H_2) is presented. Electrical energy is converted into chemical energy of syngas via nonthermal plasma (electrical energy) driven endothermic reaction. Syngas is then converted into not only CH_4, but also carbon containing liquid fuels with the existing C1 chemistry. Liquid hydrocarbon would be more preferable than synthetic CH_4 because transport and storage capability of liquid hydrocarbons is improved with great flexibilities. CH_4 and CO_2 reforming is known as dry methane reforming (DMR): CO_2 can be oxidizer as well as carbon source for C1 chemistry. There are two major problems in DMR: one is coke formation which readily deteriorates catalyst activity. The other is high temperature thermal energy is needed (above 800 °C). Therefore, combustion of initial feed is unavoidable. Nonthermal plasma enables low temperature conversion of CH_4 and CO_2 at relatively low temperature (below 600 °C), yet fast reforming is guaranteed because plasma-generated reactive species promote catalytic surface reaction. We have developed pulsed dry methane reforming as comprehensive diagnostic method of plasma catalytic methane reforming [1]. This diagnostic method is further enhanced by the combination of optical emission spectroscopy, isotope labeling, and admixture of reaction promoters. In the symposium, mechanistic study of plasma catalysis and prospects for practical application (PtG) will be presented.

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3:00pm **PS-ThA3 Plasma-based CO_2 Conversion: Experiments and Modeling**, *A. Bogaerts,* ***Ramses Snoeckx,*** University of Antwerp, Belgium **INVITED**

Plasma-based CO_2 conversion is gaining increasing interest. We try to obtain better insight in the underlying mechanisms by experiments and computer modeling. Our experiments are carried out in a (packed bed) DBD and in a vortex-flow gliding arc (GA) reactor, focusing mainly on the conversion and energy efficiency at different conditions and reactor setups. Our model calculations focus especially on the detailed plasma chemistry in a DBD, GA and microwave (MW) plasma, for pure CO_2 as well as mixtures of CO_2 with N_2, CH_4 and H_2O. For this purpose, we make use of a zero-dimensional chemical kinetics model.

When studying the plasma chemistry in pure CO_2, we focus especially on the the role of vibrationally excited CO_2 levels, which are the key species for enhanced energy efficiency of the CO_2 conversion [1].

We have also studied the plasma chemistry in CO_2/CH_4 [2,3] and in CO_2/H_2O [4] mixtures in a DBD reactor, for producing value-added chemicals. The main products formed are a mixture of H_2 and CO, or syngas, with a tuneable H_2/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds is very limited. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to improve the formation of value-added products.

Finally, we also studied the plasma chemistry in a CO_2/N_2 mixture, both in a DBD [5] and in a MW [6] plasma, to investigate the effect of this important impurity in effluent gases on the CO_2 conversion, energy efficiency and product formation. Our model and experiments reveal that N_2O and NO_x compounds are produced in the range of several 100 ppm. The reaction pathways for the formation of these compounds are again explained based on a kinetic analysis, which allows proposing solutions on how to prevent the formation of these harmful compounds.

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4:00pm **PS-ThA6 Revisiting HgCdTe Etching Mechanism in High Density CH_4-H_2 Plasmas in Terms of Langmuir Adsorption Kinetics and Taking into Account Etching Inhibition**, ***Christophe Cardinaud,*** *A. Pageau,* CNRS - IMN, France*; L. Le Brizoual,* IETR - Univ. Rennes, France*; F. Boulard, J. Baylet,* CEA, LETI, MINATEC Campus, France

In the past 20 years, intrinsic properties of $Hg_{(1-x)}Cd_xTe$ have placed this semiconductor compound as the standard material for the fabrication of high performance infrared detection devices [1]. CH_4-H_2 based plasmas have proven to be efficient to etch HgCdTe [2]. In terms of mechanism, it is usually admitted that methyl radicals, coming from the dissociation of methane CH_4, form volatile metal organic species, mainly $Cd(CH_3)_2$ and $Te(CH_3)_2$, while atomic hydrogen, coming from CH_4 and H_2 dissociation, forms volatile TeH_2, and that Hg, due to its high vapor pressure, desorbs spontaneously from the surface. Strong Cd accumulation is always observed on the processed surface, underlining that Cd removal is the limiting step of HgCdTe plasma etching. In a previous study we have identified that the surface stoichiometry change appears as soon as the etching starts and that the etch rate is closely related to the incoming flux of methyl species [3]. Consequently, the $Hg_{(1-x)}Cd_xTe$ alloy removal takes place through a Cd-rich surface layer rather than through the bulk material itself. Low-pressure high-density plasma sources and independent control of sample bias enable operation of the process with more chemical than physical etching mechanisms. Such conditions should meet the main fabrication requirements: high anisotropy, smooth sidewalls, reasonable etch rate, and low level of surface damage. However they typically fall in the HgCdTe etching / hydrocarbon deposition borderline.

Plasma-surface interaction mechanisms are investigated when varying source power, sample bias, CH_4 flow rate and total pressure. Mass spectrometry and electrostatic probes are respectively used to evaluate methyl and positive ion flux onto the surface. X-ray photoelectron spectroscopy provides surface composition. Results and etch rate measurements are discussed in the view of an ion-neutral species synergy model based on Langmuir adsorption kinetics [4] and taking into account the competition between hydrocarbon film formation and HgCdTe etching.

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4:20pm **PS-ThA7 Temporal Evolution of Surface Chemistry in Ion and Radical Dominated Etch of Hydrocarbon Polymers**, ***Barton Lane,*** *P. Ventzek, N. Eibagi,* Tokyo Electron America, Inc.*; A. Ranjan, V. Rastogi,* TEL Technology Center, America, LLC

Precise and selective etching requires the control of the chemical and physical nature of thin surface layers. We discuss here the specific example of hydrocarbon polymer etching in an argon/oxygen chemistry. An important issue is the temporal evolution of the layer started from an initial condition established by a preceding step. It is important to ascertain whether the surfaces evolve continuously or not. We find for this chemistry and film set, that there are transients which give way at longer times to

steady state conditions. Through the use of a novel *in situ* OES based technique which mimics traditional SIMS surface analysis we demonstrate the time dependent effect of argon ions on a hydrocarbon polymer surface which has been previously oxidized and separately the re-oxidation of a previously graphitized surface. Both these processes show sharp transients followed by much less active steady states. We characterize how these transients depend on the starting surface condition. We apply these same analytic techniques to the more complicated situation of the time evolution of photoresist lines which have been defined by 193i lithography. We show that the time dependence of the morphology of the surfaces of these lines which can be related to the lamellar structure of the photoresist.

4:40pm **PS-ThA8 Etching Mechanisms of Transparent Conducting Oxides by Hydrocarbon Plasmas**, ***Hu Li,*** Osaka University, Japan*; P. Friederich, K. Fink,* Karlsruhe Institut for Technology (KIT)*; K. Karahashi,* Osaka University*; M. Fukasawa, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan*; W. Wenzel,* Karlsruhe Institut for Technology (KIT)*; S. Hamaguchi,* Osaka University, Japan

Zinc oxide (ZnO) and tin-doped indium oxide (ITO) are some of the most promising transparent conducing oxides (TCOs) for optoelectronic devices such as solar panels and head-mounted liquid crystal displays. With the demand of high-resolution optoelectronic devices increasing in the market, more efficient fabrication technologies for sub-micron- or nano-scale patterning of TCOs are required. Reactive ion etching (RIE) is a key technology for such fine patterning of materials, which has been widely used in the fabrication of semiconductor devices. RIE processes for TCOs have been developed with non-corrosive gases such as CH_4. However, etching reactions and mechanisms of such processes are not fully understood yet. The goal of this study is therefore to clarify plasma-surface interactions of CH_4 based plasmas with TCOs.

It has been found in our earlier beam experiments that the etch rate of ZnO by energetic CH_x^+ ions strongly depends on the amount of hydrogen (i.e., value of *x*) of each incident CH_x^+ ion. The results have also shown that ZnO stores hydrogen after the surface was exposed to energetic hydrogen ions. The modified surface layer of ZnO, which we call a "hydrogen-embedded ZnO" layer, has a higher sputtering yield for incident (inert) ions. In this study, we have examined how hydrogen can be stored in a hydrogen-embedded ZnO layer, using *ab initio* calculations. It has been found that, when a hydrogen atom is introduced to the surface or bulk of ZnO, it forms a hydroxyl group and weakens the Zn-O bond, converting ZnO to ZnOH. The result indicates that, in terms of energy levels, ZnOH has a higher sputtering yield than ZnO. A similar discussion of hydrogen effects on ITO will be also given in this presentation.

5:00pm **PS-ThA9 The Role of the Dense Amorphous Carbon (DAC) Overlayer in Photoresist Etching**, ***Adam Pranda,*** *Z. Tomova, S. Gutierrez Razo, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Multicolor photolithography is an alternative to extreme ultraviolet (EUV) lithography in attaining device feature sizes below 10nm. The use of this technique requires modification of existing acrylate-based photoresists in order to enable selective photochemistry with multiple wavelengths of light. In the following work, we establish the viability of multicolor photoresists by comparing their plasma etching behavior to industry-standard 193nm and 248nm photoresists.

The 193nm and 248nm photoresist polymers commonly used in industry are abundant in C-H bonds that scission when exposed to high energy ions that are characteristic of plasma etching. The rapid removal of volatile hydrogen- and oxygen-based carbon products results in the formation of a dense amorphous carbon (DAC) overlayer in the nm range. Steady-state etching of the bulk photoresist entails the constant removal and reformation of this overlayer, and the DAC layer acts as an etch-inhibiting layer on top of the bulk resist. The overall density of the overlayer will determine the etching behavior of the underlying photoresist.

In this work, we define a baseline for comparing multicolor photoresists by investigating the relationships between chamber conditions, formation of the DAC overlayer, and the resultant etch yields for a poly(methyl methacrylate)-based 193nm photoresist polymer (PR193) and a polystyrene-based 248nm photoresist polymer (PR248) using an inductively-coupled plasma (ICP) reactor as well as an electron cyclotron wave resonance (ECWR) reactor. The thickness and refractive index of both the DAC overlayer and bulk photoresist layer were monitored in real-time using *in-situ* ellipsometry.

We observe a correlation between the ambient chamber oxygen concentration, magnitude of the DAC overlayer refractive index (reflective of material density), and photoresist steady state etch rate. In the absence of ambient oxygen, the primary steady-state etching mechanism is physical sputtering. In the presence of ambient oxygen, the etching mechanism has contributions from physical and chemical sputtering, the latter mainly through adsorbed oxygen on the sample surface. Removal of carbon from the overlayer is enhanced by chemical sputtering, resulting in a less dense DAC overlayer which yields a higher steady state etch rate compared to the oxygen-deficient condition. These observations are useful as a baseline for evaluating the behavior of multicolor photoresists and provide a benchmark to guide which photoresists to synthesize to achieve the desired etching behavior.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309).

5:20pm **PS-ThA10 Transport Mechanism on Reactive Species in Downflow Reactors for F-based Etch**, ***Kenji Ishikawa,*** *T. Tsutsumi, Y. Zhang, M. Sekine, T. Hayashi, M. Hori,* Nagoya University, Japan*; Y. Horiike,* Tsukuba University, Japan

In chemical dry etching (CDE) of F-based etch chemistry such as CF_4, SF_6, etc. [1], it has been believed that F atoms transport as long as 1 meters downflow of plasma source and etch Si with etch rates around 500 nm/min [2]. The etch results for SiO_2 and SiN films were shown stable even low rates but relevant values regardless of the distance [3,4]. Otherwise, whilst the cases of NO + F_2 gas mixture generates F atoms, the etch rates significantly decreases with the distance from the location generated F atoms [5]. These apparently paradoxical results remain an open question, which needs to revisit. In particular of O_2 addition, the etch rate-dependence versus distance is evident, thus the the effects of peroxy radicals, OOF, and peroxides, F_2O_2, are hypothesized. Here, we report the transport mechanism on reactive species in downflow for F-based etch.

The chemical dry etching apparatus was constructed by a long-length quartz tube. A mixture of CF_4 and O_2 gases was flown into the tube and a microwave cavity (2.45 GHz, 50W) was used for plasma generation. At the downflow, F atom or FOO signals were measured by electron spin resonance (ESR) instrument [6,7]. Quantum-chemical calculations were done with B3LYP/6-311+G(d) by Gaussian 09.

Ground-state of O_2 ($^3\Sigma g$) is reacted with F atom and stabilized 0.36 eV to generate OOF. Subsequently, OOF reacts with F atom to form F_2O_2. The OOF and Si reaction takes place Si + OOF -> SiF + $O_2(^3\Sigma g)$, rather than Si-oxidation pathways.

Experimentally, concentrations of F atoms at downflow depended on mixture ratio of O_2 and distances from the plasma source. The O_2 addition enhanced to transport F atom toward further positions. In general, although F atom recombination to F2 is known to be relatively low reaction rate, however the recombination cannot be negligible during transport. Thus, we revisited the radical complex mechanism, i.e., F + O_2 -> OOF and OOF -> F + O_2, *vise verse*. In summary, we suggest that the transport of reactive species needs to revisit effects of the radical complex of F atom with O_2., in particular of the O_2 added F-based chemistry.

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5:40pm **PS-ThA11 Surface Reactions of Magnetic Materials by CO Cluster Beams**, ***Kazuhiro Karahashi,*** Osaka University, Japan*; T. Seki, J. Matsuo,* Kyoto University, Japan*; K. Mizotani, K. Kinoshita, S. Hamaguchi,* Osaka University, Japan

Dry etching of magnetic thin films is a critical issue in the fabrication of magnetic random access memories (MRAMs). Currently argon (Ar) ion milling seems the only etching technique available in the manufacturing processes. However Ar ion milling is incapable of achieving anisotropic and selective etching of magnetic films and therefore extensive research is underway to establish highly selective anisotropic reactive ion etching (RIE) processes for magnetic thin films [1]. The formation of volatile metal carbonyl compounds produced by reactions of a metal surface with incident CO molecules may be used as a chemical etching process but such reaction probabilities are known to be very small. In this study we propose gas cluster beam processes as a means to etch magnetic metal surfaces. Gas clusters can provide a large number of reactant molecules to the metal surface at low incident energies and are expected to cause multiple collision processes at impact [2]. Especially we have examined surface

reactions of Ni thin films by CO neutral clusters as well as energetic CO ion clusters. First we studied Ni etching reaction by incident CO cluster ion irradiation with typical single cluster ion energy being $E_{cluster}$ = 20 keV (and a single CO molecule ion incident energy being E_{CO}= 11 eV). It was found that amorphous carbon deposition occurred on Ni surfaces and the beam did not etch the Ni films. These results suggest that each CO cluster is broken apart to CO molecules at impact by the excessive kinetic energy. Such excess kinetic energy prevents the formation of carbonyl compounds. Second, we examined interactions between low-energy incident CO neutral clusters ($E_{cluster}$ = 300 eV, E_{CO}= 60 meV) with Ni surfaces. NiCO (Mass 86), which are fragments of nickel carbonyl compound [$Ni(CO)_4$], were detected with a quadrupole mass spectrometer equipped in the chamber of the beam system. These results suggest that carbonyl formation reaction occurred by CO neutral cluster irradiation. Currently the probability of such carbonyl-formation reaction seems low and we shall discuss how the carbonyl-formation reaction rate on a metal surface can be increased. This work was supported by the Semiconductor Technology Academic Research Center (STARC)

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6:00pm **PS-ThA12 A Method to Accelerate Creation of Plasma Etch Recipes Using Physics and Bayesian Statistics**, ***Meghali Chopra***, *R.T. Bonnecaze,* The University of Texas at Austin

Creating and optimizing plasma etch recipes for microelectronic and other nanostructured devices is costly and time consuming. Fully optimized plasma etch recipes can take several months to two years to create, which slows time to market. Here we introduce a method combining physics-based global plasma models, Bayesian statistics and experimental data to rapidly develop and optimize recipes for plasma etching. The method predicts optimal process windows with two- to three-fold fewer experiments than using factorial design of experiments. We first demonstrate this method for prediction of etch rates in CCP and ICP-RIE plasma reactors. These predictions are then successfully compared to synthetic and experimental data. We next use the method to determine the anisotropic etch rates through a single material including level set modeling. Lastly, we apply the method to the etch recipe development of a high aspect ratio trench through a multi-layer stack. Our results show that we can reduce three-fold the cost and time required to develop an etch recipe.

Plasma Science and Technology
Room Hall D - Session PS-ThP

Plasma Science and Technology Division Poster Session

PS-ThP1 RF Assisted Reactive High Power Impulse Magnetron Sputtering Deposition of Titanium Nitride Thin Film for Plasmonic Applications, ***Ru-Jing Sun***, National Tsing Hua University, Taiwan, Republic of China; *B.H. Liao, C.-N. Hsiao,* Instrument Technology Research Center, Taiwan, Republic of China; *K.C. Leou,* National Tsing Hua University, Taiwan, Republic of China

Titanium nitride (TiN) films have attracted a great deal of interests recently for applications in plasmonic devices in near-infrared wavelengths range. Here we report the optical properties of the TiN films prepared by using radio frequency power assisted reactive high power impulse magnetron sputtering (HIPMS) deposition technique. The TiN films were grown on either Si or glass substrates for a thickness up to 400 nm. A spectroscopic ellipsometer was used to measure the refraction index (n) and extinction coefficient (k) of the films. Measurements results show that, depending on the deposition conditions, the optical properties of the TiN films vary over a wide range, from those of typical TiN film as deposited by conventional magnetron sputtering, to those of metallic copper or gold. Sheet resistance of the film was also measured by hall-effect method and strong correction between the optical and the electrical properties are demonstrated. Results from XRD analysis also reveal that the lowest film resistivity occurs for TiNx film with a stoichiometric composition, as expected. These results demonstrate that one can fine tune the optical property of TiN film by simply controlling the deposition conditions to meet the requirements of optical devices.

PS-ThP2 Transport Line for Laser Multicharged Ion Implantation and Deposition System, ***MdHaider Shaim***, *M.M. Rahman, O. Balki,* Old Dominion University; *A. Sarkissian,* Plasmionic Technologies; *M.L. Korwin-Pawlowski,* University Du Quebec en outaouais, Canada; *H.E. Elsayed-Ali,* Old Dominion University

Components of a transport line for a laser multicharged ion (MCI) source are constructed and tested. These components are an einzel lens for ion focusing, parallel deflection plates for multicharged ion selection, electrostatic cylindrical ion energy analyzers for MCI energy-to-charge *E/z* selection, three-grid energy analyzer, and Faraday cup for time-of-flight ion detection . Aluminum and carbon MCIs are generated by a nanosecond Nd:YAG laser (wavelength 1064 nm, pulse width 7.4 ns) ablation of a target in a vacuum chamber. Time-of-flight and a three-grid retarding ion energy analyzers are used to determine the velocity and the charge state of the MCIs. A three-electrode cylindrical einzel lens is used to focus the MCIs. At a distance of 30 cm from the center of the focusing electrode of the einzel lens, Al^{1+} and Al^{2+} has a minimum beam diameter of ~1.5 mm, while for Al^{3+} and Al^{4+} the minimum beam diameter is ~2.5 mm. Simulation of the ion trajectories was done using SIMION 8.1. A high voltage pulse applied to a set of two parallel deflecting plates is used for the pickup of ions with different charge states according to their time-of-flight. The electrostatic ion energy analyzer combined with the time-of-flight measurement are used to resolve both *E/z* and *z* and obtain the energy distribution of each charge. The Overall energy resolution of the electrostatic ion energy analyzer for carbon MCI is 7 – 9%.

PS-ThP5 Optimizing Process Parameters for Plasma Assisted Atomic Layer Epitaxy (PA-ALE) of Nitrides, ***Virginia Anderson***, *D.R. Boris, N. Nepal, S.D. Johnson, A.C. Kozen,* Naval Research Laboratory; *Z. Robinson,* Boston University; *S.C. Hernandez, C.R. Eddy, Jr., S.G. Walton,* Naval Research Laboratory

III-Nitride (III-N) binary compounds (InN GaN and AlN) are attractive semiconductor materials for a wide range of device applications. Plasma assisted atomic layer epitaxy (PA-ALE) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. In this work we employ optical emission spectroscopy and charged particle collectors to characterize an inductively coupled plasma on a commercial atomic layer epitaxy tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions of argon and nitrogen. The objective is to diagnose optimum conditions for the production of N* radicals in the plasma source, believed to be most useful for the growth of III-N films, and correlate these changes in N* production with changes in film characteristics.

PS-ThP6 Plasma Treatment of Plated Surfaces, ***Christopher Fields***, *M.J. Buie,* Coherent Inc

Plasma treatment is used increasingly in vacuum applications to ensure removal of surface level micro-contamination which may prevent or inhibit bonding or joining applications. [1-4] We have characterized via a designed experiment the changes to the surface after plasma treatment. Stainless steel 304L was chosen as the flange material for the study. One surface was milled to provide at a minimum surface finish of 16 m in. A thorough characterization of the material was performed prior to plating including surface roughness measurements using an optical profilometer. Pre-plating results show a surface with 'race track' grooves around the sealing surface. The optical profilometer measured a surface roughness of 12 m in and a total roughness profile height of 105 m in. The flanges were plated with a decorative bright nickel, nickel sulfamate and a combination of the two films. The plating thickness varied from 0.5 mil to 1.5 mil. Samples were treated with either an ultrasonic aqueous clean, a plasma clean or a combination of the two. The flanges were then measured for ionic contamination via ultra-pure water extraction ion chromatography. Elemental analysis was performed using x-ray photoelectron spectroscopy (XPS). The data reveals an effective plasma treatment which removes all traces of carbon and minimizes Na. Additionally, plasma parameters were optimized in order to minimize surface roughening during processing.

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PS-ThP7 Customizing Arrays of Microplasmas for Controlling Properties of Electromagnetic Waves, ***Chenhui Qu***, *P. Tian, M.J. Kushner,* University of Michigan

Arrays of microplasmas are being investigated to manipulate electromagnetic waves. Such applications require control of the electromagnetic properties of individual plasma cells. Motivated by the tradeoff between fast response and high plasma density, the optimum operating range for the plasma includes pressures from 10s to 100s Torr, and so the scale of each cell shrinks to 100s μm due to *pd* scaling. Controlling cross-talk is a major challenge in design of microplasma arrays since plasma cells are not separated by physical barriers as in conventional plasma-display-panels. This lack of physical barriers is necessary in order to reduce the loss or scattering of incident electromagnetic waves.

Small 2-dimensional arrays of microplasmas are being computationally investigated with the goals of maximizing electron densities while minimizing cross-talk between plasma cells. The microplasma arrays are sustained in 10s to 100s Torr of rare gas mixtures excited by dc-unipolar pulses. The small arrays contain 4 to 9 plasma cells.

The base case geometry contains four plasma cells operating in 60 Torr Ar powered by 300 V peak value unipolar pulses having a 10 MHz pulse repetition frequency and 30% duty cycle. The width of the array is 320 μm and the length is 830 μm, conditions which produce maximum electron densities up to 2×10^{14} cm^{-3} with a cathode fall region forming near the exposed cathodes. Beam ionization by secondary electrons contributes ≈65% of the total ionization during the pulse on period. Cross-talk between plasma cells does not significantly affect the performance of individual plasma cells even though they are not physically isolated. The predicted plasma properties are used to evaluate the potential for controlling electromagnetic wave properties when propagating through large arrays of such microplasmas. The electromagnetic simulator HFSS was used to investigate microwave propagation through the microplasma array, including control of the magnitude and polarization of the electric field.

Work was supported by Air Force Office of Scientific Research, Department of Energy Office of Fusion Energy Science and the National Science Foundation.

PS-ThP8 Optical Emission Diagnostics of a Non-equilibrium Helium Plasma Jet at 1 Atm in Ambient Air, ***Tam Nguyen***, *E. Hernández, D.J. Economou, V.M. Donnelly,* University of Houston

Non-thermal atmospheric pressure plasmas are of interest for their potential use in surface treatment and biomedical applications. Even though considerable progress has been made, less is known about the species generated in close proximity to a surface. A novel approach using optical emission spectroscopy (OES) has been developed to probe emissions close to the surface. The plasma jet splays along the flat face of a hemispherical quartz prism. Emission was observed through the prism as a function of the angle of incidence. In this manner, emission integrated from a line-of-sight across the jet was obtained. Emission was also recorded as a function of angle through a MgF_2 window coupled to a VUV spectrometer. At normal incidence (0^o), light was detected mainly from the discharge within the plasma source, which consisted of a quartz tube surrounded by two electrodes, powered by a 200 kHz AC source. He emission at 706 nm peaked twice per cycle, near the positive and negative voltage maxima. Conversely, VUV-UV-visible emissions from H, O, N, OH, NO and N_2^+ impurities contained in the He feed gas within the discharge were hardly modulated. The only exception was N_2(C-B) emission, which peaked strongly near the maximum positive voltage and weakly near the maximum negative voltage. When the angle of incidence was reduced to just below the critical angle (43.4^o) to observe the region within ~1 mm of the surface, all emissions were strongly modulated and peaked near (lead or lag) the maximum positive voltage; no emission was detected at the maximum negative voltage. All of these observations are consistent with excitation of O, N, OH, H, and NO being predominantly due to dissociative excitation of precursors O_2, N_2, H_2O and NO_2 resulting from collisions with He metastables (He*). Similarly, N_2^+ emission was attributed to He* Penning ionization and formation of excited N_2^+. Only He 706 nm and N_2(C-B) emissions were due to electron impact excitation. Inside the discharge tube, He* is long lived because it is quenched very slowly by diffusion to the walls or by collisions with He or electrons, hence He*-induced emission are only weakly modulated. Near the surface, air diffuses into the He and leads to rapid He* quenching and hence a strong modulation of the emissions.

PS-ThP9 Etching Capability of Silicon Nitride using a Low Electron Temperature Plasma Source, ***Hiroyuki Miyazoe***, *A.V. Jagtiani, S.U. Engelmann,* IBM T.J. Watson Research Center*; D.R. Boris, S.C. Hernández, E.H. Lock, S.G. Walton,* Naval Research Laboratory*; E.A. Joseph,* IBM T.J. Watson Research Center

The ability to achieve atomic layer precision is among the ultimate goals envisioned for plasma etching technology. Electron beam generated plasma (Large Area Plasma Processing System: LAPPS) as developed in the Naval Research Laboratory (NRL) is one such candidate to realize these process goals [1]. We have been demonstrating process feasibility for single layer graphitic carbon films such as graphene and carbon nanotubes (CNTs), which have unique properties, making them well-suited for studying the ability to process with atomic layer precision and assess impact of plasma damage. [2] In this work, we explore SiN etching using pulsed, electron beam generated plasmas produced in Ar/SF_6 and Ar/O_2 mixtures. The impact of process parameters such as relative gas concentration, duty factor, and substrate bias on the etch rates and selectivity (vs. carbon films, silicon and silicon oxide) has been investigated. The results indicate the ability to achieve etch rates lower than 50 nm/min, depending on material, suggesting the potential for surface engineering with monolayer precision. We also investigated tight pitch patterning of SiN films using LAPPS. Etching of »10nm-thick SiN at 60 nm pitch with minimized line roughness was demonstrated. Taken together, this work suggests electron beam generated plasmas are a promising route toward atomic layer processing. This work is partially supported by the Naval Research Laboratory base program.

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PS-ThP10 Deep GaAs Etching with V-shaped Trench Profile Using Inductively Coupled Plasma Technology, *T. Sugahara,* SAMCO Inc., Japan*;* ***Shogo Uehara***, SAMCO Inc.*; M. Hiramoto,* SAMCO Inc., Japan

There is an ongoing demand for device miniaturization, and at the same time, improvement of the die yields per wafer. For die separation with brittle wafer materials such as Gallium Arsenide (GaAs), Indium Phosphide (InP), and Gallium Nitride (GaN), a diamond tipped tool is widely used for the scribe and break process. Using a diamond tipped tool provides deep V-shaped scribe lines with a sharpened point profile on the bottom. However, this scribing method may cause die chipping, and also limits the minimum width of the streets between die. Wet etching can fabricate a V-shaped scribe line with a sharpened point profile on the bottom, but its depth is limited to just a few hundred nanometers [1], and is not deep enough to break substrates that are a few hundred micrometers thick. As an alternative to scribing with the diamond tipped tool or wet etching, plasma scribing technology offers a chipping-free process solution with deep scribe lines and narrow street widths for higher die yields. Additionally, batch processing of multiple wafers by the plasma scribing technology enables higher throughput than other techniques. However, conventional GaAs deep plasma etching processes yield scribe lines with a rounded bottom profile, and the rounded bottom makes the die separation irreproducible. In order to make die separation more precise and reliable for plasma scribing, the trench profile of scribe lines needs to be a V-shape with a sharp bottom profile.

In this research, an Inductively Coupled Plasma (ICP) etching technology suitable for GaAs die separation was developed to achieve a V-shaped trench with sharp bottom profile. Scribing and breaking of GaAs depend on the orientation of the scribe lines on the GaAs surface. The GaAs wafers used for this experiment had a <100> crystal orientation, and were 350 µm thick. A 10 µm wide photoresist mask and chlorine chemistry were used to etch 50 µm deep trenches with a sharp point profile at the bottom. The GaAs etch rate was 9.6 µm/min and the etch selectivity of GaAs over photoresist was approximately 10:1. In the investigation of the relationship between the etch depth and the trench profile, it was found that the bottom flat of the trench shrinks in size from the initial trench width, as the trench depth increases.

The V-shape with the sharp point profile on the trench bottom enables reproducible plasma scribing of GaAs wafers, minimal street widths between die and minimal damage to the die upon die separation.

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PS-ThP12 Ion Beam Etch Process Optimization for the Patterning of High Density STTRAM Pillars, ***Vincent Ip***, Veeco*; S. Huang,* Lam Research Corporation*; S.D. Carnevale,* Veeco*; I.L. Berry,* Lam Research Corporation*; K. Rook,* Veeco*; T.B. Lill,* Lam Research Corporation*; A.P. Paranjpe, F. Cerio,* Veeco

STTRAM device patterning has been demonstrated via either: reactive ion etch followed by ion beam etch (IBE); or by a full IBE strategy.[1],[2] The patterning of high density STTRAM structures requires detailed process optimization, due to multiple requirements including: high aspect ratio; avoidance of shorting across the MTJ barrier; and minimization of damage to the active layers of the structure. We discuss methods to address each of these challenges under a full IBE patterning scheme. For large CD structures, with wide pitch, a single-step IBE recipe may be sufficient, but for small CD or tight pitch features, a multi-step IBE process appears to be necessary.

The primary consideration during the first etch step(s) is to effectively open up the pattern, while minimizing re-deposition across the tunnel junction. We present experimental IBE etch rates for typical STTRAM stack and hard mask materials versus: incidence angle; ion species (Neon, Argon, Xenon); and ion energy. We utilize these etch rates combined with 2-D etch simulations, to present guidelines for etching of STTRAM pillars with mask height ~ 150 nm, and pitch varying from 80 – 800 nm. The simulations capture etched feature shapes and spatial distribution of redeposited material. We show that re-deposition can be minimized by: etch angle further from normal incidence; using lower mass ion; and/or higher ion energy.

The primary consideration during the final etch step(s) is to remove any sidewall damaged layer resulting from the earlier step(s), while minimizing further damage.[3] We present 3-D etch calculations and SRIM simulations to provide guidelines for the damage cleanup steps, in terms of optimal etch angle, and optimal ion species and energy.[4] We show that sidewall damage cleanup is maximized by etch angle further from normal, while further damage generation is minimized primarily by lower ion energy. In particular, we present minimum ion energies required to maintain specified damaged layer thicknesses from <1nm upwards.

We simulate optimized combinations of multiple etch steps, and demonstrate effective patterning of pillars of 80 nm pitch, resulting in feature sidewalls with ~ 85^o sidewall angle and no metal re-deposition across the tunnel junction.

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PS-ThP13 Down Stream Plasma Ash Process Impact on Metal Electrode Oxidation and Nitridation for 10nm and Below Logic Technology, *B. Elliston, G. Kishko, V. Vaniapura, V.P. Nagorny,* ***Shawming Ma,*** Mattson Technology

For the semiconductor process flow with advanced nodes below 10nm, it is desired to remove the photoresist on top of metal electrodes, such as TiN, with minimum oxidation and nitridation. In general, the resist is typically removed by plasma strip followed by wet clean or by plasma strip or wet strip only. To minimize and control the oxidation, it is desired to use a non-oxygen chemistry. In this paper, detailed surface characterization methods including surface sheet resistance (Rs), optical ellipsometry, X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) are used to evaluate the surface oxidation and nitridation under various hardware and process conditions. It is identified that the grounded Faraday shield is critical to reducing tube erosion from the Inductive Coupled Plasma (ICP) coil's strong electric field which may an contribute to less wafer surface oxidation. Current modeling suggests the tube's erosion from high electric fields inside the source may contribute small amounts of oxygen that induces more wafer oxidation on wafers, even when a non-oxygen chemistry is used. In addition, extended que times can affect the post oxidation measurements . Possible hardware and process solution are also discussed to minimize metal oxidation and nitridation.

PS-ThP14 Atomic Layer Etching of Conventional and 2D Materials, ***Mike Cooke**, A.L. Goodyear, R. Sundaram, B. Halsall,* Oxford Instruments Plasma Technology, UK

How close can a real plasma etcher come to delivering ideal atomic layer etch (ALE)? We describe hardware studies into the limits of using conventional plasma etch tools to perform cyclical self-limiting etch processes, especially the chemical stability of the chamber and the electrical reproducibility of short RF plasmas. Self-limiting behaviour is not in itself evidence of single layer etching: silicon ALE etch rates are shown to depend strongly on chamber history.

The promise of ALE to etch single atomic layers is tested by using an optimised etch tool to etch 2D materials, grown by CVD. Raman spectroscopy of MoS2 few-layer films before and after a cyclical etch process are presented.

PS-ThP15 Rapid *In Situ* H Plasma Carbon and Oxygen Cleaning of $In_{0.53}Ga_{0.47}As(001)$ and $Si_{0.5}Ge_{0.5}(110)$, *S. Wolf, M. Edmonds,* University of California at San Diego*; X. Jiang,* PIE Scientific*; R. Droopad,* Texas State University*; N. Yoshida, L. Dong,* Applied Materials*; R. Galatage, S. Siddiqui, B. Sahu,* GLOBALFOUNDRIES*; A.C. Kummel,* University of California at San Diego*;* ***Mahmut Kavrik,*** University of California San Diego

InGaAs and SiGe have demonstrated good potential to replace silicon in MOS devices due to their intrinsically high mobilities. In order to implement these compound semiconductors into devices, the surfaces of these materials must be atomically flat and void of surface defects, which can be accomplished by performing one of several surface cleaning techniques available: RCA standard cleaning procedure consisting of various treatments with NH_4OH, H_2O_2, HF, HCl, and H_2O to remove the native oxide and organic and ionic contaminants, UV/ozone treatments, and cleaning via thermal gas crackers and plasma sources. However, wet processing can leave organic residues and a thin layer of native oxide on the surface due to exposure to ambient conditions, while the vacuum/dry processing steps can take over 30 minutes to perform. A technique that overcomes these issues involves the use of in-situ hydrogen plasma to remove carbon and oxygen present on the surface. In this study, X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition of the $In_{0.53}Ga_{0.47}As(001)$ and $Si_{0.5}Ge_{0.5}(110)$ surfaces before and after plasma exposures. To optimize the conditions for cleaning with a plasma source, the effect of plasma power and pressure on carbon cleaning and oxygen contamination were determined. In addition, the effect of pure H_2 versus an H_2/Ar mixture was investigated in relation to the removal of carbon and oxygen contaminants. Using the described approach, a two second H plasma clean removed all carbon and oxygen from the $In_{0.53}Ga_{0.47}As(001)$ surface while minimally etching the surface, and nearly all carbon and some oxygen were removed on the $Si_{0.5}Ge_{0.5}(110)$ surface. The SiGe surface is more difficult to clean because it is more sensitive to oxygen than the InGaAs surface and can easily be explained by the high heat of formation of SiO_2. In effect, the high heat of formation for SiO_2 poses two challenges for cleaning of the surface: (1) trace O_2 or H_2O in the plasma gas are likely to form more Si-O bonds and (2) breaking Si-O bonds by atomic H will be unlikely. By incorporating the in-situ downstream plasma source and optimized experimental conditions, the efficacy of ion-less plasma treatment for the rapid cleaning of the $In_{0.53}Ga_{0.47}As(001)$ and $Si_{0.5}Ge_{0.5}(110)$ surfaces has been demonstrated.

PS-ThP17 Backside Via Last Process Technologies for Wafer Level 3D Stacking., ***Toshiyuki Sakuishi**, T. Murayama, Y. Morikawa,* ULVAC Inc., Japan

The number of devices connected to the internet has been increasing year by year. Not only Smartphone and Tablet PC, Devices for IoT (Internet of Things) are expected to increase rapidly. Data traffic is increasing exponentially and the data centers are required to be high speed data processing and low power consumption. Required performances are high bandwidth/bandwidth density, low latency, increased data processing speed, expanded data storage. These are desired to achieve without increasing cost. For multifunctionality and downsizing, heterogeneous integration is essential technology. To achieve these requirements, the backside via-last process is very important. We have been developing Si deep RIE technique and process integration that are optimized for via-last TSV formation. Our etching process is mainly non-Bosch etching using SF6/O2 based gas. To realize high rate etching, high density F radical is necessary. In addition, the Non-Bosch etching performs etching and sidewall protection simultaneously, so proportion of F and O radical is important. Key technology to achieve a uniform proportion of F and O radical is multi-ICP (Inductively Coupled Plasma) source. Our etching source newly developed shows excellent performance in Non-Bosch etching, but also adapts to Bosch etching. Our Non-Bosch etching is better to taper angle controllability. Tapered shape and smooth sidewall improve the deposition coverage and reduce the TSV formation cost. New Si deep RIE technique using multi-ICP source opens the way to new 3D packaging technology.

PS-ThP18 New Deep SiO_2 Etching Process Issues for Silicon Photonics Device Fabrications, ***Keizo Kinoshita**,* PETRA, Japan*; M. Noguchi,* PETRA*; T. Horikawa,* AIST*; T. Nakamura, T. Mogami,* PETRA

Silicon Photonics (SiPh) is a promising technology for wide-band and large-capacity data communications. The SiPh chip needs to embed laser diodes (LD's) for optical communication. In our approach, LD's have to be mounted on a pedestal structure [1, 2]. To fabricate the pedestal structure, 5 μm deep SiO_2 hole should be patterned by a deep etching process.

A 300 mm CCP etch system was applied to etch the SiO_2 layer. Photoresist (PR) patterns with 4.6 μm thick were developed by a KrF lithography system. Ar diluted fluorocarbon gas chemistries were adopted. Three etch-selectivity conditions for the SiO_2 against the PR were examined. Significant etch residues over the etched surface were observed under a relatively high etch selectivity condition. In contrast, the sample etched under a relatively low etch selectivity condition showed no etch residues, but showed conspicuous striations at the sidewalls of SiO_2 which can cause optical coupling loss of the SiPh devices. These deep SiO_2 etching issues as a function of the etch selectivity can be discussed qualitatively.

Under the high etch selectivity condition, deposited fluorocarbon polymer and etch by-products over the chamber walls increase generally. They can re-deposit over the wafer surface during etching, and cause the etch residue. The amount of the deposition (*DP*) can be expressed as follows,

$DP = f(t)$,

where t is total etching time, and f is a function which reflect the etch selectivity. Higher the etch selectivity is, larger the *DP* is. The etch residue issue will happen when the *DP* value exceeds some threshold. This is a common issue in fabricating both CMOS and SiPh chips.

On the other hand, the etching under the lower etching selectivity condition brings about larger damages on PR polymer by bond breaking and desorption of functional groups, and causes the large line edge roughness (*LER*) of the PR pattern which will be transferred to the striation during etching. The *LER* can be expressed as follows,

$LER = g(t)$,

where g is a function related to the etch selectivity reflecting protective ability for the PR. Higher the etch selectivity is, smaller the *LER* is at the same t. This issue is apparent for the SiPh chip fabrication.

Therefore, it is important to minimize *DP·LER* products within some threshold in the deep SiO_2 etching process developments for the SiPh devices. And, we succeeded in the deep SiO_2 etching by the *DP·LER* products minimization approach.

This work was supported by NEDO. The authors thank staff members of SCR station in AIST for their technical support. [1] T. Shimizu, et al., Photon. Res., 2, A19 (2014). [2] K. Kinoshita, et al., AVS 62th Int. Symp., PS-ThP8, p. 51, (2015).

PS-ThP20 Modeling of Remote Plasma Sources using CFD-ACE+*, **Abhra Roy**, P. Shukla, K. Jain, A.N. Bhoj,* ESI US R&D Inc.

Remote plasma processing typically involves plasma generation in a main chamber and the substrate activation (or etching or deposition) by plasma activated species outside the plasma zone to reduce damage to the substrate. The remote substrate location also enables control of plasma properties to a sufficient degree to preferentially result in a desired flux of species to the substrate. The CFD-ACE+ modeling platform can be used for simulations of remote plasma sources to address gas flow, heat transfer, plasma physics and chemistry and electromagnetics in a coupled fashion. In this paper, we report on computational modeling studies of plasmas sustained in Ar/N_2 and Ar/NF_3 mixtures using global and 2D simulations. The Kinetic Module of CFD-ACE+ is used to generate the electron energy distribution function (EEDF) and compute electron impact reaction rates and transport coefficients. The fast global models help isolate the major reaction pathways and help reduce the number of reaction steps of the volumetric mechanism for multidimensional simulations. At these pressures of interest, the back diffusion of injected Ar into the plasma zone results in activation of reaction pathways that result in feedstock dissociation. The effect of mixture ratios, power, frequency and pressure on the resulting plasma, ion and radical densities in the main reactor chamber, and fluxes of plasma species at the remote substrate are discussed.

PS-ThP21 Controllable Deposition of TiO_2 Films by Atmospheric Pressure Dielectric Barrier Discharge: Gas Composition Effect and Mechanism*, **Qianqian Chen**, A. Ozkan, S. Collette, J. Mertens, J. Baneton, M.P. Delplancke, F. Reniers,* Université Libre de Bruxelles, Belgium

In this work, various controlled morphologies of TiO_2 films are synthesized by atmospheric pressure argon/oxygen dielectric barrier discharge (DBD) using titanium tetraisopropoxide (TTIP) as precursor. The gas compositions for the formation of TiO_2 films are optimized by adjusting the flow rate of plasmagen gas from 0 to 9.5 L/min, while keeping the flow rate of TTIP and O_2 as constant. The morphology of the deposited films is observed by Scanning Electron Microscopy (SEM). It is found that the morphologies change from columnar film to dense film as the flow rate of plasmagen gas increases. The chemical structures and properties of the deposited films are characterized by means of Infrared Reflection-Absorption Spectroscopy (IRRAS), Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS). The results show that the films are amorphous with similar chemical compositions. The plasma properties are investigated using Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS). The intensity of Ar* species increase as the flow rate of plasmagen gas increases, which indicates that the concentration of Ar* species have a strong effect on the morphology of the TiO_2 films. The MS measurements show that H^+, O^+, H_2O^+, CO_2^+, $C_3H_6O^+$ and a weak signal of TiO_2^+ are produced in the plasma. The mechanisms of the TiO_2 films formation from TTIP by DBD are discussed.

PS-ThP22 Synthesis of Acrylate Coatings with Tunable and Permanent Wettability by Atmospheric Plasma*, B. Nisol, J. Guesquière, **Delphine Merche**, N. Vandencasteele, F. Reniers,* Université Libre de Bruxelles, Belgium

Plasma polymerization is an eco-friendly route (low temperature, solvent-free process) used to prepare functional thin films with desired properties (e.g aesthetics coatings, protective coatings against corrosion and abrasion, coatings for adhesion and barrier properties…) on any kinds of substrates. In this study, transparent acrylate coatings were synthesized by PECVD under atmospheric pressure, from the simultaneous injection of acrylic acid (AA) and propargyl methacrylate (propaMA) into a dynamic DBD, using argon as the carrier gas.

The influence of the ratio AA/propaMA and the power on the physical and chemical properties of the coatings deposited onto various substrates (Si wafers, polyolefins films and thick gold films) was highlighted by WCA (wettability), mechanical profilometry (thickness), XPS and FTIR-IRRAS (chemical composition).

The addition of propaMA to AA allows reaching high deposition rates (up to 11 nm/sec) thanks to its highly unsaturated (and reactive) nature.

WCA results evidenced the possibility to tune the surface wettability from highly hydrophobic (140° for the pure propaMA coatings) to highly hydrophilic (15° for the pure AA coatings). Moreover, the coatings were very stable over time and were seen not to suffer from hydrophobic recovery. Indeed, the WCA remained constant for at least a period of 2 months.

The highly hydrophobic character of pure propaMA coatings is due to an important texturization of its surface, as revealed by scanning electron micrographs (SEM); the high reactivity of propaMA is thought to induce gas-phase polymerization, and to the subsequent formation of globular features. Also, in the explored conditions, smooth coatings could only be obtained for high AA proportions in the gas mixture.

XPS and FTIR results revealed the presence of alcohol and ketones groups in addition to the carboxylic/esters functions of the monomer precursors. The COOR groups related to the presence of carboxylic acid increase with the proportion of AA in the AA/propaMa mixture while the C-O and C=O groups decrease.

Thanks to excellent ageing properties, such thin and transparent coatings represent a promising alternative to polymer surface plasma functionalization.

We would like to thank the Belgian Federal Government IAP-(interuniversity program) "Physical Chemistry of Plasma Surface Interactions" P7/34, and the Walloon Region.

PS-ThP23 A High-flux Low-energy Hydrogen Ion Beam Using an end-Hall Ion Source*, **Jacqueline van Veldhoven**, E. te Sligte, J.P.B. Janssen,* TNO Technical Sciences, Netherlands*; I. Ament,* Carl Zeiss SMT GmbH, Germany

Most ion sources that produce high-flux hydrogen ion beams, particularly gridded sources, perform best in the high energy range (keV) [1]. Alternatively, some plasma sources produce very-low-energy ions (<< 10 eV). However, in an intermediate energy range of 10-200 eV, to our knowledge, there are no hydrogen ion sources that produce high-flux beams.

Despite this absence, we believe such a source would be of interest to a variety of fields, such as surface passivation and treatment [1-3], solar winds [4], fusion reactors [5], and EUV sources [6].

A typical ion source that is known for its high fluxes at the relevant ion energy range is the end-Hall ion source. This source produces good results with argon and oxygen [7], but no report of it being used with hydrogen was found. This contribution shows the use of an end-Hall ion source with hydrogen. Both the flux and the ion energy distribution of the ion beam were measured using a Retarding Field Energy Analyzer (RFEA) for different settings of the source and at different positions.

At the lowest discharge voltage and highest discharge current where the signal is still stable (100 V, 4A), a maximum hydrogen ion flux of $8.2 \cdot 10^{19}$ ions/m^2/s was measured at an energy range of ~0-130 eV and at a distance of 11 cm.

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PS-ThP24 A System of Radical Probes for Plasma Characterization, ***Dren Qerimi,*** University of Illinois at Urbana-Champaign; *I.A. Shchelkanov,* University of Illinois at Urbana Champaign; *D.N. Ruzic,* University of Illinois at Urbana-Champaign

The current state-of-the-art methods to identify presence of radical species in vacuum chambers are optical methods, which suffer from the lack of spatial resolution and require expensive optical equipment. Center for Plasma Material Interactions (CPMI) at the University of Illinois aims to develop a probe array (catalytic probe) to measure concentration of reactive gas spices in low temperature plasma with high temporal and spatial resolution. Radical probes as plasma diagnostic device will be used to determine plasma parameters in helicon plasma source. The basic principle and advantage of a probe array is that is has several sensitive elements capable to distinguish between different gas species. The sensitive element has a size of several millimetres with a nanostructured chemically sensitive to specific reactive gas species surface. The nanostructured surface is positioned right on top of a thermocouple [1]. The nanostructured probe surface provides efficient recombination of active species with subsequent energy release as a heat. The system consists of additional two probes, first to obtain the overall heat flux on probe array, and the second is a reference probe with surface chemically active to all gases. The thermocouple detects the heat released after recombination and gives immediate voltage signal output. The array of several probes is capable to distinguish between different gas species with sub centimeter spatial resolution. The probes give accurate results in a broad range of reactive species concentrations from about 10^{19} to 10^{22} m^{-3}.

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PS-ThP25 Using Optical Emission and Broadband Absorption Spectroscopy to Elucidate Energy Partitioning Trends Within Inductively Coupled Plasma Systems, ***Angela Hanna,*** *J.M. Blechle, E.R. Fisher,* Colorado State University

A fundamental understanding of interactions between plasma species is essential to characterizing complex plasma chemistry phenomena. By utilizing various optical spectroscopy techniques to probe internal energetics within nitrogen and oxygen-containing plasmas, we have elucidated energy partitioning information for both ground and excited state plasma species. Our approach focused initially on characterizing internal energies of N_2 within a simple homonuclear diatomic system (N_2). We then broadened our study to include the slightly more complex N_2O system and also a mixed gas plasma system (N_2 and O_2). In these systems, both N_2 and NO molecules can be studied. Optical emission spectroscopy (OES) and broadband absorption spectroscopy (BAS) techniques were employed to study internal energies of both excited and ground state species in all of these systems. Characteristic plasma energies (e.g. electron temperatures (T_e) and small molecule vibrational and rotational temperatures [$T_v$and T_r, respectively] were determined for species formed within each system. In most cases, T_v is significantly higher than T_r for molecules such as N_2 and NO, with T_v ranging from ~2000 K to >3000K and T_r having values between ~300 K and 1000 K. In general, vibrational and rotational temperatures show a strong positive correlation with applied rf power and often display a negative correlation with system pressure for the precursors studied. Deviations from these trends have also been investigated. Additional data from more complex systems used to modify a range of materials such as catalyst particles will also be presented. Collectively, these data enable insight into the properties of various plasma systems and the role energy partitioning plays in the assessment of plasma chemistry.

PS-ThP27 Modeling of Electron Kinetics in rf Discharges at Low and High Pressures, ***Ananth Bhoj,*** *Z.A. Xiong,* ESI US R&D Inc.; *V.I. Kolobov,* CFD Research Corporation

Low temperature plasmas (LTPs) are used for numerous applications over a wide range of gas pressures from a few mTorr up to ambient pressures (760 Torr). Simulations of LTPs involve the multiphysics coupling of gas flow, heat transfer, plasma physics, volumetric and surface chemistry and electromagnetics. For CAE models like CFD-ACE+, to accurately capture the plasma physics, a kinetic treatment is often important for different plasma species. In particular, while the mean free paths and the energy relaxation lengths for ions and neutrals are similar, they differ vastly for electrons. This memory effect for elastic collisions of electrons with neutrals has a profound influence to electron kinetics. The kinetic treatment for electrons assumes significance because the electron energy distribution function (EEDF) in highly non-Maxwellian in most cases, and the electron-induced reaction rates are sensitive to the tail of the EEDF. At very low pressures, global models that assume diffusion dominated electron transport with conservation of total energy are useful to quickly estimate plasma characteristics and trends in RF systems. In this approach, the EEDF depends on the total electron energy and energy dependence is obtained by spatially averaging the Fokker-Planck (FP) equation for the EEDF. At intermediate pressures, the tail of the EEDF becomes local, whereas the rest of the EEDF remains non-local. In this regime, the isotropic part of the EEDF depends both on energy and space, so nonlocal effects must be explicitly accounted for by solving the FP equation. Such EEDF nonlocality behavior has been shown to extend up to pL = 10 Torr-cm. Beyond this range, fluid models with non-Maxwellian EEDFs based on lookup tables are computationally more efficient and capture the physics well. We show examples of simulations in these various regimes using CFD-ACE+.

PS-ThP29 Nanoparticle Synthesis via a High Voltage Pulsed DC Atmospheric-Pressure Microplasma Jet, ***Steven Doyle,*** *K.G. Xu,* University of Alabama in Huntsville

A high voltage pulsed DC microplasma jet operating at atmospheric pressure has been developed for nanoparticle synthesis applications. The configuration consists of a high voltage center pin electrode inserted in a quartz tube, running between 5kv – 10kv. The plasma forming gas, being argon, is fed into the tube along with a small concentration of methane, which serves as the working gas. Flow rates and methane ratios vary between 2 – 5 slm and 0.01/Ar – 0.05/Ar, respectively. Nanoparticles of interest include both metal oxides and carbon. Metal oxide nanoparticle formation comes from the oxidation of the center pin electrode, while carbon nanoparticles are a product of the decomposition of the methane working gas. The impact of the center pin electrode chemical composition on the resulting nanoparticles has been tested. The main properties of interest for the nanoparticles are the size, shape, and population density. Copper, tungsten, and mechanical pencil graphite were chosen as the three most desirable electrodes based on the literature. Finally, the flow rates and voltages of the system have been adjusted to further demonstrate their impact on the nanoparticles formed. The nanoparticles are imaged with an SEM and the chemical compositions are confirmed via EDS analysis. The system generates a “cold” microplasma with a gas temperature of just over 300 K. This property makes the microplasma system design of great interest for applications where low temperature limits exist.

PS-ThP30 Extending the Volume and Processing Area of Atmospheric Pressure Plasma Jets, ***Eric Gillman,*** *D.R. Boris, M.H. Helle, S.C. Hernández, Tz.B. Petrova, G.M. Petrov, S.G. Walton,* Naval Research Laboratory

Atmospheric pressure plasmas have certain advantage in materials synthesis and processing that are not available with other approaches including low-pressure plasmas. In particular, the breadth of reactions afforded by non-equilibrium, low temperature plasmas is unique; plasmas produced in full density air allows one to extend the application space to systems and materials that are not vacuum compatible. Non-equilibrium, atmospheric pressure plasma jet devices are well-suited for such applications given their relatively simple design and modest power requirements. However, their size tends to limit their utility to small scale processes and treatments. In this work, we describe approaches to extend the volume of non-equilibrium, atmospheric pressure plasma jets and thus, surface area that can be treated. In particular, we consider geometric and gas flow solutions to increase volume without increasing power requirements. We use high-speed cameras, optical emission spectroscopy (OES), current and voltage measurements, and simulations to characterize the results and understand the potential for and/or limitations to scale-up. This work is supported by the Naval Research Laboratory base program.

PS-ThP31 Characteristics of Cutoff Probe for Magnetized Plasma Measurement, ***Jung-Hyung Kim,*** Korea Research Institute of Standards and Science, Republic of Korea; *K.H. You,* Korea Research Institute of Standards and Science; *S.J. You,* Chungnam National University; *H.C. Lee, D.J. Seong,* Korea Research Institute of Standards and Science

We investigate the transmission spectrum of a cutoff probe in magnetized plasma using a circuit simulation and experiment. The circuit simulation was calculated using a permittivity tensor that can be changed depending on the direction of the magnetic field and electric field which is generated by radiating antenna of the cutoff probe instead of a permittivity of non-magnetized plasma. The experiment was performed at various probe directions and magnetic field strength while maintaining the plasma density constant. When the magnetic field and electric field are same

directions, the measured cutoff frequency can be used for the plasma frequency (f_{pe}) same as non-magnetized plasma results. However, electric field is perpendicular with the magnetic field, the measured cutoff frequency can be considered for upper hybrid frequency ($f_{uh} = (f_{pe}^2 + f_{ce}^2)^{1/2}$). All results are consistent with a circuit simulation results.

PS-ThP32 Development of the Gas Cherenkov Detector (GCD-3) and the Unique Engineering Challenges Associated with the ASME Boiler and Pressure Vessel Code, ***Frank Lopez***, *H.W. Herrmann, J.A. Oertel, S.H. Batha, Y.H. Kim, J.R. Griego, T.N. Archuleta, R.J. Aragonez, V.E. Fatherley, C.S. Young, A. Hsu, R.M. Malone,* Los Alamos National Laboratory

The development of the LANL Gas Cherenkov Detector (GCD-3) fielded at the Laboratory for Laser Energetics OMEGA laser facility generated significant engineering challenges. The GCD-3 is a third-generation gas Cherenkov diagnostic that provides important information about Inertial Confinement Fusion (ICF) implosions including fusion burn and imploded capsule conditions. The GCD-3 utilizes CO_2, SF_6 and C_2F_6 gases separately pressurized at 400psig to provide the scintillation media. Unique experimental objectives contrasted with the requirements of the ASME Boiler and Pressure Vessel (B&PV) Code resulted in diverging pressure vessel concepts throughout the design process. In addition, a facility-specific weight limitation and stringent fluorinated gas leak rate requirements added to the complexity of the diagnostic's development. Specifically, achieving a vessel/detector weight limit of 100 pounds in conjunction with a maximum fluorinated gas leak rate of 1X10E-9 STD cc/second (helium) at 1 atmosphere differential pressure proved to be challenging. As such, Conflat knife-edge crushed-metal seals were an essential aspect of the design. The LANL Pressure Safety Program in compliance with DOE Order 10CFR851 invokes the ASME Boiler and Pressure Vessel Code, Section VIII, Division I and II for the design of all pressure vessels. As the B&PV Code can be characterized as a "one size fits all" standard, the tendency toward conservatism is typical. Vessel wall and flange thicknesses are routinely substantial, although inconsequential to refineries, are atypical of pressurized ICF diagnostics. A detailed summary of these design challenges correlated with the resulting experimental results bring emphasis to the successful collaborative mix of engineering and physics expertise within the ICF diagnostic development arena.

PS-ThP33 Magnetic Tunnel Junctions Etch and Encapsulation Process Optimization for High-Density STT-MRAM Applications, ***Laurent Souriau***, *D. Radisic, S. Kundu, V. Paraschiv,* imec, Belgium*; F. Yamashita, K. Fujimoto, S. Tahara, K. Maeda,* TEL, Japan*; W. Kim, S. Rao, G. Donadio, D. Crotti, D. Tsvetanova, J. Swerts, S. Mertens, T. Lin, S. Couet, D. Piumi, G.S. Kar, A. Furnemont,* imec, Belgium

STT-MRAM is being extensively developed as a potential candidate to replace conventional memories due to its unique characteristics: fast speed, non-volatility and excellent endurance. One of the major challenge for high-volume, high density STT-MRAM fabrication remains the patterning of the Magnetic Tunnel Junction (MTJ). Practically, the metals used in the MTJ stack hardly form any volatile compounds with conventional etching plasmas often resulting in strong re-deposition of metals on the sidewall (SW) of the junction and hence shorting of the device. Moreover, MTJs manifest strong sensitivity to any form of chemical or physical damage caused by plasma processing leading to degradation of the electrical/magnetic performance of the fabricated memory cell. The focus of this work is to develop a Reactive Ion Etching based patterning process in combination with SW engineering by oxidation and in-situ encapsulation to mitigate those issues. We demonstrated patterning of MTJ down to 30nm, in pitch down to 200nm with excellent electrical yield and very limited performance degradation.

The MTJ patterning process has been developed on a TACTRAS platform from Tokyo Electron Limited using a dual-frequency capacitive coupled plasma reactor specially customized for STT-MRAM application as well as a microwave plasma CVD reactor to deposit Si_3N_4. A TiN metallic hard mask has been used to pattern the CoPt or CoNi based MTJs with perpendicular magnetic anisotropy. The patterning consisted of a 2-step sputtering based etch process. The first etch was carried out with Ar to define the MTJ pillar while the second etch used Kr to efficiently remove metallic residues from the MTJ SWs. Noble gases were used in order to avoid chemical damage. The patterning was followed by an in-situ mild oxidation of the MTJ SWs to passivate metallic residues as well as the peripheral damaged zone caused by ion bombardment. Finally, a Si_3N_4 encapsulation was applied in-situ to protect the MTJ from air exposure.

We demonstrated isolated pillar size down to 30nm as well as 45nm pillars at a 200nm pitch. Tight RP distribution (σ~4%) was achieved demonstrating that pillar size was uniform across the wafer surface and the MTJ short were efficiently circumvented. Limited degradation (<10%) of the TMR as function of pillar size was achieved. A yield of more than 97% was achieved in Mbit array with less than 0.5% cells exhibiting electrically shorted behavior and the 2.5% remainder of the cell being not switchable. The optimization of the Si_3N_4 encapsulation process to improve the thermal stability of the device post processing will be discussed at the conference.

PS-ThP34 Effect of High DC Bias on Silicon Oxide Coatings Deposited by Plasma Enhanced Chemical Vapor Deposition, ***Norihiro Jiko***, Kobe Steel, Ltd., Japan*; A. Narai,* Kobe Steel, Ltd.*; N. Kawakami, T. Okimoto,* Kobe Steel, Ltd., Japan

It is well known that electronic devices such as organic light emitting diode and electronic paper are degenerated by water vapor and oxygen that penetrate from air. Therefore polymer substrates, which are expected to replace glass substrates for their flexibility and light weight but are permeable to water vapor and oxygen, are required to be coated with gas-barrier layers such as Silicon oxide (SiOx). In addition to the high barrier property, it is necessary for practical use to suppress curl of the polymer substrates caused by the coating with high stress.

Plasma enhanced chemical vapor deposition (PECVD) is one of the industrial-scale coating techniques of the SiOx layers with high barrier performance (see, for example, ref. 1). It has been reported that for the deposition of the SiOx layers using PECVD, ion bombardment plays an important role to densify the layers and improve the barrier performance, through experiments in which SiOx layers are deposited with DC bias applied at the substrate [2]. However curl of the polymer substrates tends to be enhanced by a high compressive stress of the SiOx layers caused by a strong ion bombardment and is required to be controlled.

The objective of this study is to explore the possibility of compatible high density and low stress through experiments in which SiOx layers were deposited with a wide range of DC bias. SiOx layers were deposited using a PECVD system. The substrate silicon wafers (4 inch in diameter) were mounted on a 400kHz RF applied electrode (6 inch in diameter). The power was varied to yield DC bias from 0 to -1.2kV. 13.56MHz RF was inductively coupled into the chamber with a planar-coiled RF antenna through a quartz window with an applied power kept at 300W. Hexamethyldisiloxane and oxygen were introduced into the chamber at a pressure of 4Pa.

The density of the SiOx layers examined with a X-ray reflectometer increased with enhancing DC bias from 0 to -360V, and it remained almost constant for higher DC bias. On the other hand, compressive stress measured with a profilometer steeply increased from DC bias of 0 to -200V and then reduced gradually to the highest DC bias investigated, which is in contrast to the above-mentioned constant density for high DC bias. These results suggest that the high bias enables a desirable polymer substrate with a SiOx barrier layer. Detailed analysis of the SiOx layers to comprehend these bias dependent phenomena will be reported at the presentation.

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