Energy Frontiers Topical Conference
Room: Mesilla - Session EN+PS-MoM

Plasmas for Photovoltaics & Energy Applications
Moderator: B. Lane, TEL Technology Center America

8:20am **EN+PS-MoM1 Combinatorial Plasma CVD of Si Thin Films with a Multihollow Discharge Plasma CVD Reactor**, ***M. Shiratani***, *K. Koga, T. Matsunaga, Y. Kawashima, W. Nakamura, G. Uchida, N. Itagaki*, Kyushu University, Japan

A-Si and micro-crystalline thin films for solar cells are widely deposited by plasma CVD in industry. To realize combinatorial plasma CVD of such Si thin films, we have developed a multi-hollow discharge plasma CVD method, by which fluxes of H and SiH_3 as well as their flux ratio on the substrate placed perpendicular to the electrodes depend on the distance from the discharges [1-4]. Thus, we can simultaneously deposit Si thin films with various structures and properties. For 60 MHz discharges of H_2+SiH_4 (0.3%), no films were deposited just near the discharge regions due to Si etching by H, micro-crystalline films were deposited in a rather narrow area around the no film regions, and a-Si:H films were obtained in the rest wide area far from the discharges. The spatial distribution of film structures indicate that the density ratio of H to SiH_3 decreases sharply with increasing the distance from the discharges and the surface reaction probability of H is much higher than that of SiH_3, being consistent with the reported surface reaction probabilities [5, 6]. For 2-6 Torr, the micro-crystalline film structure such as crystalline volume fraction and grain size varies sharply not only along the direction perpendicular to the electrodes but also along the direction parallel to the electrodes. These results suggest that the micro-crystalline film structure is highly sensitive to spatial and temporal uniformity of fluxes of H and SiH_3 as well as their flux ratio.

[1] K. Koga, et al., Jpn. J. Appl. Phys. **44,** L1430 (2005).

[2] W. M. Nakamura, et al., IEEE Trans. Plasma Sci. **36**, 888 (2008).

[3] W. M. Nakamura, et al., J. Phys.: Conf. Series **100**, 082018 (2008).

[4] H. Sato, et al., J. Plasma Fusion Res. SERIES, **8**, 1435 (2009).

[5] A. Matsuda, et al., Surface Sci. **227**, 50 (1990).

[6] J. Perrin, et al., J. Vac. Sci. Technol. A, **16**, 278 (1998).

8:40am **EN+PS-MoM2 Infrared Solar Cells Using Plasma-Processed Carbon Nanotubes**, ***T. Kaneko***, *S. Kodama, Y. Li, R. Hatakeyama*, Tohoku University, Japan

Since the conventional silicon solar-cell conversion is limited to a certain window of solar cell photon energies over 1 eV, a full use of the solar spectrum is one of the crucial issues in order to greatly increase the solar cell efficiency. In this sense, carbon nanotubes (CNTs) are attracting much interest for photovoltaic energy conversion because of their broad absorption bands including the infrared range (0.2 ~ 1.3 eV) as well as other advantages such as large surface areas, high mobility of charge carrier, high mechanical strength, chemical stability, and so on. In this connection, we have developed a plasma-ion irradiation method, which enables pristine single-walled carbon nanotubes (SWNTs) to selectively encapsulate various kinds of atoms and molecules, such as metals and fullerenes, serving as electrons donors or acceptors inside their cavities. Then these enhanced p-type, n-type, and pn-junction housed semiconductor-SWNTs are applied toward the realization of high-efficient photovoltaic devices, which is composed of thin films of p- and n-types semiconductor SWNTs or an individual SWNT with p-n junction inside. Here, as a first step, electrical properties of p-n junctions fabricated using a combination of the thin films of pristine (empty) SWNT or C_{60}-encapsulated SWNT (C_{60}@SWNT), and n-doped Si (n-Si) are investigated.

The electrical properties of these SWNT film/n-Si devices show an obvious rectifying characteristic, and a short-circuit current I_{SC} and an open-circuit voltage V_{OC} through a downward shift of *I-V* curves are observed under illumination of light with wavelength of 1550 nm which corresponds to the photon energy of 0.8 eV. Moreover, it is found that the device fabricated with the C_{60}@SWNT film has a larger V_{OC} caused possibly by a large diffusion voltage in the interface of p-n junction compared with the device fabricated with the pristine SWNT film, due to the enhanced p-type behavior of SWNTs after C_{60} encapsulation. To investigate undesirable photovoltaic effects of n-Si, we fabricate a schottky barrier solar cell consisting of silver (Ag) and n-Si in the absence of SWNTs. It is confirmed that the Ag/n-Si schottky barrier solar cell generates photo currents in the visible range (1.5 ~ 3 eV), while there is almost no difference between with and without light in the infrared range (0.8 eV) because the light with photon energy less than 1 eV cannot be absorbed by Si.

Based on these results, high performance solar cells which work in the infrared region are for the first time demonstrated to be formed using SWNTs, especially p-type enhanced C_{60}@SWNT.

9:00am **EN+PS-MoM3 A Novel Method of Controlling Plasma Uniformity in a Large Area VHF Plasma Source for Solar Applications**, ***T. Tanaka***, *J. Kudela, E. Hammond, C. Boitnott, Z. Chen, J.A. Kenney, S. Rauf*, Applied Materials Inc. **INVITED**

Processing a large area substrate in a capacitively coupled plasma (CCP) reactor is becoming increasingly more difficult as the driving frequency required by the process is becoming higher and the size of the substrates is becoming larger. At the VHF (very high frequency) range the wave length of the driving signal is approaching the size of the substrate, and the resulting standing wave causes a severely non-uniform process. In this presentation, we will present a novel approach using magnetic boundary conditions in conjunction with phase modulation between multiple power feed points to improve process uniformity for a CCP reactor operating in the VHF range. The substrate size we consider is Gen 8.5 (2.2 m × 2.6 m substrate) and the VHF power applied to generate the plasma is 40 and 60 MHz. At 60 MHz, with the vacuum wavelength of 5 m, the size of the substrate is approximately ½ of the vacuum wavelength. An electromagnetic simulation with a pseudo plasma showed that, when 60 MHz is applied in a conventional manner, i.e. it is fed from the center of the back of one of the electrodes, it generates a dome shape electromagnetic field profile, which falls off sharply to almost zero at the voltage node before rising again towards the edges. A similar field pattern was also generated even when the VHF was fed from two feed points located at the opposing edges. The plasma distribution pattern measured with a 4 × 8 grid of optical emission spectroscopic (OES) probes revealed that the plasma was localized in the center when VHF the signal applied to the feed points were in phase. To modify the wave propagation pattern to change the shape of the standing wave in the central area, we placed ferrite material along two of the edges (edges that are away from the feed points) of the powered electrode. In this case, the peak in the central area was significantly stretched towards the ferrite-lined edges. We also found that the stretched “bar” of plasma could be moved over the substrate area by dynamically modifying the relative phase between the feed points in a manner similar to the technique employed by Yamakoshi *etal*. [1], and effectively distribute the processing plasma to much larger area.

[1] H.Yamakoshi *etal*. Appl. Phys. Lett. 88, 081502 (2006)

9:40am **EN+PS-MoM5 Novel Plasma Processing Routes of Si Nanocrystals for Photovoltaic Applications**, ***İ. Doğan***, *N.J. Kramer, MA. Verheijen,* Eindhoven University of Technology, Netherlands*, T.H. van der Loop,* University of Amsterdam, Netherlands*, A.H.M. Smets,* Eindhoven University of Technology, Netherlands*, T. Gregorkiewicz,* University of Amsterdam, Netherlands*, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Photovoltaic applications have been developed mostly on silicon technology in order to generate electricity from solar energy by efficient conversion of solar spectrum. In this work, we have focused on the novel processing routes of Si nanocrystals (Si-NCs) in a remote expanding thermal plasma (ETP). Si-NCs were formed inside a SiH_4-Ar plasma by excessive heating of SiH_x clusters via electron and ion collisions. Formation routes of nanoparticles were investigated under different conditions by changing SiH_4 and Ar flow rates, deposition pressures and arc currents. The morphologies of the deposits were powder-like, consisting of densely packed crystalline particles and inter-space of amorphous Si. Due to the variations in plasma regions from center to side walls, the powder color and properties were different on the different parts of the deposited samples. The formation of nanoparticles on these parts was investigated by a number of diagnostic techniques. As a first exploration, transmission electron microscopy (TEM) and Raman spectroscopy (RS) measurements have been carried out. It was confirmed by both TEM and RS that the particle size and morphology was varying throughout the film. For most of the samples, nanoparticles seemed to be mixed in size but the general tendency is to have smaller size distributions from central part to the outer part of the films. Formation of crystalline structures was confirmed by X-Ray diffraction (XRD) with Si(111) peaks. It was also shown by photoluminescence spectroscopy (PL) that the optical emission was in the visible range and shifts with respect to size difference of Si-NCs. Size distribution as a function of PL emission energy has been demonstrated for particles less than 8nm. TEM was employed to investigate the size distribution of the larger particles which was around 50nm. The responsible mechanism in the plasma leading to a systematic change on the particle size was discussed by

means of electron and ion density, and particle residence time. Getting a good control on the plasma conditions and particle size makes it possible for manipulating Si-NCs to higher packing densities in thin films which makes them suitable for photovoltaic devices such as down converters based on multi-exciton-generation (MEG).

10:00am **EN+PS-MoM6 Characterisation of Thin Film CdTe Multilayer Photovoltaic Devices Deposited by Closed Field Magnetron Sputtering**, *J.K. Bowers, S. Moh, A. Abbas, P.N. Rowley, H.M. Upadhyaya,* ***J.M. Walls***, Loughborough University, UK

A new magnetron sputtering strategy is introduced that utilises high plasma densities (~5mA.cm^{-2}) to avoid or reduce high temperature processing. The technique uses magnetrons of opposing magnetic polarity to create a "closed field" in which the plasma density is enhanced without the need for high applied voltages. A batch system has been used which employs a rotating vertical drum as the substrate carrier and a symmetrical array of four linear magnetrons. The magnetrons are fitted with target materials for each of the thin films required in the photovoltaic (PV) stack viz. CdTe absorber layer, CdS buffer layer, metal contact and the back transparent conducting oxide (TCO) contact using the superstrate configuration. The "closed field" sputtering technology allows scale up not only for larger batch system designs but it is also configurable for "in-line" or "roll to roll" formats for large scale production. The morphology of each of the layers is characterised together with the overall device performance.

10:40am **EN+PS-MoM8 Material Properties of Hydrogenated Nanocrystalline Silicon Thin Films by RF-PECVD using He-SiH$_4$ Mixture**, ***I.K. Kim***, *J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Hydrogenated nanocrystalline silicon (nc-Si:H) and amorphous silicon thin film are expected to be promising

materials for solar cell and thin film transistor. Especially, nc-Si:H thin films have been reported to have

an enhanced stability due to its more rigid structure. These thin films are usually grown with

plasma enhanced chemical vapor deposition (PECVD) using silicon-containing gas mixtures such as SiH_4 and H_2.

To increase the photovoltaic efficiency and to improve the mobility of TFT devices, it is necessary to produce

nanocrystalline silicon films with higher crystallization percentages. But it is reported that high H_2. dilution leads to

a significantly lower deposition rate.

In this study, we investigated the influence of He mixture with SiH_4 gas instead of H_2 to improve the crystallization

percentage of the deposited silicon without significantly decreasing the deposition rate.

To find out properties of the thin film deposited with He/SiH_4 such as structural properties, crystalline volume fraction (Xc), active radicals in plasma, Si-H bonding characteristics, and conductivity, Scanning Electron Microscopy

(SEM), Raman spectroscopy, Optical Emission Spectroscopy (OES), Fourier-Transform-Infra-Red (FT-IR), and Keithley

measurement kit, were used respectively. The results showed the increase of crystallization percentage by using

He instead of H_2 as the additive gas and, with the increase of the applied RF power up to 140W, crystalline volume

fraction of about 80% could be observed.

11:00am **EN+PS-MoM9 Surface Composition and Gas-Phase Passivation of Plasma-Synthesized Si Nanoparticles**, ***B.N. Jariwala****, Colorado School of Mines, *N.J. Kramer,* Eindhoven University of Technology, Netherlands, *B.G. Lee, P. Stradins,* National Renewable Energy Laboratory, *M.C.M. van de Sanden,* Eindhoven University of Technology, Netherlands, *C.V. Ciobanu, S. Agarwal*, Colorado School of Mines

Tunable band gap of c-Si nanoparticles (NPs) (<5 nm) along with the possibility of multiple exciton generation has led to an increased interest in this form of Si as a material for 3rd generation photovoltaic (PV) devices. In addition to a high degree of control over the particle size, surface passivation of the NPs is key to their utilization in PV applications. In this presentation, we will primarily focus on understanding the growth of Si NPs in a dusty plasma, determining the surface composition of the NPs, and demonstrating novel techniques for passivation and encapsulation through the gas-phase. The particles are grown in a SiH_4/Ar plasma generated in a tubular flow rf discharge. The plasma source is attached to an in-house-built vacuum chamber equipped with *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and a quadrupole mass spectrometer. Using this technique, we have synthesized Si NPs in the size range of 3-7 nm, which transition from amorphous to crystalline over the rf power range of 5 to 40 W. The *in situ* IR data show that the surface hydride composition of the NPs is related to their crystallinity, which in turn depends on particle heating during synthesis. The as-synthesized NPs surfaces are terminated with Si mono-, di- and tri-hydrides. The higher hydride concentration decreases with increasing particle crystallinity, similar to previous observations on the amorphous Si surfaces, where higher Si hydrides are known to decompose with increasing deposition temperatures. These results also are consistent with the particle heating models proposed for dusty plasmas. In the first surface passivation approach, the as-synthesized H-terminated Si NPs, which oxidize even under high-vacuum conditions, are passivated *in situ* through hydrosilylation using 1-alkenes of different chain lengths. We have used density functional theory calculations to investigate the detailed reaction mechanism for various alkene chain lengths, and to understand the effects of alkene coverage on the oxidation of the surface. The surface reaction kinetics for hydrosilylation is observed *in situ* by monitoring the C-H and Si-H stretching vibrations. The ligand coverage is determined to be roughly 50% of the surface sites, which is sufficient to prevent oxidation for several hours. The quality of surface passivation is further determined through the photoluminescence quantum yield measurements, which show a higher yield for surface passivated NPs. In the second approach, the NPs are passivated with metal oxides using atomic layer deposition that involves the two different oxidation steps with O_3 and H_2O to achieve deposition at <200 °C.

11:20am **EN+PS-MoM10 Effects of Hole-Array-Electrode on the Characteristics of Radio Frequency Capacitively Coupled Plasma Sources for uc-Si Thin Film PECVD**, ***H.-J. Lee****, S.-S. Wi,* Pusan National University, Republic of Korea, *D. Kim, D. Hwang, W.S. Chang*, LG Electronics, Republic of Korea

In order to improve the productivity of thin film growth in rf capacitively coupled plasma based chemical vapor deposition system, modifications of electrode surface geometry has frequently been used. Array of holes in the shower head electrode is probably the most popular one. In this paper, using self-consistent fluid approximation with collisional sheath model, we have analyzed the effects of the hole array on the plasma characteristics in terms of plasma density, electron temperature, ion current density, sheath voltage and electron heating efficiency. It is shown that electron heating efficiency of the hole array electrode increases more than 10 % compared with that of flat electrodes. DC bias voltage at the substrate side increases with hole depth and pitch due to increase in surface area ratio between powered and substrate electrode. Peak electron density near throat region of the hole structure becomes more than 2 time higher than that of flat parallel electrode at the same voltage driving condition. It was experimentally verified that these variations of plasma properties is beneficial for high rate of Si thin film deposition

11:40am **EN+PS-MoM11 Arc Energy in Large Scale Magnetron Sputtering**, ***D. Carter****, H. Walde*, Advanced Energy Industries, Inc.

A detailed analysis of sputtering arcs on a large scale (3400 cm^2) magnetron source reveals some common trends related to energy absorbed in these events and the progression of current and voltage through their duration. Examination of these trends provides insight into the rapid release of arc energy and some of the practical limitations of the techniques used to minimize their impact on deposition processes. Two very different but equally important materials were studied, metallic aluminum and ceramic, aluminum-doped, zinc oxide. While the characteristics and behaviors of arcs from these two materials are generally similar, subtle distinctions in the evolution of current and voltage explain a significant difference in measured arc energies. These observations present factors for consideration regarding arc suppression and also raise the question of what is the minimum achievable arc energy. In an attempt to answer this fundamental question a stored energy model for a large scale magnetron system is proposed. Using practical assumptions for sheath capacitance and source inductance, minimum arc energy is calculated to serve as the ultimate goal for a next generation arc detection and suppression system.

* Coburn & Winters Student Award Finalist

Plasma Science and Technology
Room: Aztec - Session PS-MoM

Advanced BEOL / Interconnect Etching I
Moderator: K. Kumar, TEL Technology Center America

8:20am **PS-MoM1 Plasma Processes Challenges for Porous SiOCH Patterning in Advanced Interconnects**, ***N. Posseme***, CEA-LETI-MINATEC, France, *T. Chevolleau,* CNRS-LTM, France, *T. David,* CEA-LETI-MINATEC, France, *M. Darnon,* CNRS-LTM, France, *F. Bailly, R. Bouyssou, J. Ducote, C. Verove,* STMicroelectronics, France, *O. Joubert*, CNRS-LTM, France **INVITED**

The choice of copper/Low-k interconnects architecture is one of the keys for integrated circuits performances, process manufacturability and scalability. Today, the implementation of porous low-k material becomes mandatory in order to minimize the signal propagation delay in the interconnections. In this context, the traditional plasma processes issues (the plasma-induced damages, dimension and profile control, selectivity) and new emerging challenges (sidewalls surface roughness, dielectric wiggling) become the critical points to control the reliability and defectivity.

Based on plasma-surface interaction understanding, the main issues and also the potential solutions will be illustrated through different process architecture using metallic or organic hard masks strategies.

9:00am **PS-MoM3 TiN Selectivity Improvement by DC Voltage Effect in a DC+ Dual Frequency Capacitive Coupled Plasma Etcher**, ***M. Nishino****, M. Honda, Y. Ooya, R. Shimizu*, Tokyo Electron AT Limited, Japan

Metal Hard Mask(TiN) damascene scheme has been chosen by many logic semiconductor manufacturers for 2x or beyond BEOL processes. Due to issues related to Aspect Ratio, wiggling, and integration with low mechanical stress resistant porous low-k dielectric materials, TiN hard mask has become thinner and less resistant to etch. As the technology node decreases to sub 20nm, Self-Aligned Via(SAV) process will be introduced for MHM dual damascene scheme to maintain Via CD within the confined specifications of the MHM. With this scheme, TiN MHM is exposed to RIE etch twice: once during partial via formation and another in trench etch. Due to such tight process margins, many semiconductor manufacturing companies are focusing on high selective chemistry for TiN during both Via and Trench dielectric etch process. The DC+ Dual frequency etcher is a capacitive coupled plasma etcher with a superimposed DC voltage. This configuration has been proven to be more effective for maintaining TiN hard mask during dielectric etching. A negative DC bias is applied to the upper Si electrode. The Si electrode surface reacts with CFx radicals from fluorocarbon based plasma and the fluorine component of bulk plasma was reduced. This phenomenon is the interaction between fluorocarbon based plasma and Si electrode which was induced by DC voltage. This paper presents an investigation of TiN hard mask high selective process from this interaction. We measured Ne and Vdc areas of MHM trench process both with and without DC voltage conditions and investigated the direction of Ne/Vdc windows as MHM trench process at first . We evaluated this interaction effect from Ne and Vdc trend with DC voltage and observed that DC voltage did not only acquire higher TiN selectivity to dielectric (maintain TiN thickness) but also reduce TiN HM facet etching rate (control CD shift) in dielectric etching. This is one of the advantages for the DC+ Dual frequency capacitive coupled plasma etcher .

9:20am **PS-MoM4 RIE Process Challenges in sub 30nm node Trench First Metal Hard Mask Scheme**, *K. Zin,* ***Y. Feurprier****, Y. Chiba, H. Kida,* Tokyo Electron Limited, *M. Ishikawa,* Toshiba America Electronic Components, *Y. Mignot,* STMicroelectronics, *Y. Yin*, IBM Systems and Technology Group

As scaling of microelectronic devices approaches sub 30nm nodes, many material and module process challenges in BEOL plasma patterning have been reported. One of the methods that has gained traction over recent years for enabling sub 20nm feature patterning is the Trench First metal Hard Mask (TFmHM) scheme. While this scheme solves or mitigates many challenges that are inherent with Via First Trench Last (VFTL) Scheme, it introduced other dielectric RIE process and hardware challenges. One of the root causes of the former is the fact that all patterns and materials are exposed to plasma at the same time. As such, the simultaneous control of via, trench and chamfer profiles (i.e. Critical Dimensions, depth, taper profile, etc), the need to control selectivity between multiple patterning layer (TiN, TEOS, ULK, Barrier cap, etc), and ULK damage control has become more pertinent in the dielectric etch. As the direct result of such tight process guidelines, the hardware challenges arise and new dimensions in process controls are needed. The prolonged exposure of the TiN to the plasma created the need for more robust production worthy hardware. The required selectivity of the materials necessitate temperature controllable chucks. The more complex patterning techniques require ULK preservation and other uniformity controls. In this paper, the RIE efforts on process controls of the profiles, material selectivity, associated hardware challenges and possible future roadmaps under TFmHM scheme will be discussed.

This work was performed by the Research team at TEL Technology Center America in joint development with IBM Research Alliance Teams in Albany, NY.

9:40am **PS-MoM5 BEOL Double Patterning: Challenges for Etch**, ***Y. Yin****, J.C. Arnold, M. Colburn, S. Burns, S. Holmes, C. Koay,* IBM Systems and Technology Group, *R. Kim,* Global Foundries, *G. Landie,* STMicroelectronics, *D. Horak,* IBM Systems and Technology Group, *Y. Mignot,* STMicroelectronics, *H. Tomizawa*, Toshiba Corporation

10:40am **PS-MoM8 Film Diffusivity-Dependent Role of VUV/O_2 and Ar^+ Ions in SiCOH Ultra-low-*k* Dielectric Films**, ***J. Lee****, D.B. Graves*, University of California, Berkeley

The degradation of porous ultra-low-*k* material, like SiCOH, under plasma processing continues to be a problem in the next generation of integrated-circuit fabrication. Due to exposure with many species during plasma treatment, such as photons, ions, radicals, etc., it is difficult to identify the mechanisms responsible for plasma-induced damage. Some studies have attempted to decouple plasma-generated species in order to study the effect of individual components and possible synergistic effects [1,2]. Using a vacuum beam apparatus with a calibrated VUV lamp and Ar ion gun, we show that 147 nm VUV photons and the presence of molecular O2 cause a loss of methylated species in SiCOH, creating a silica-like structure on the upper layer of the exposed material. The extent of the VUV/O2 induced damage as well as the effect of Ar ion bombardment is dependent on the interconnectivity, and thus diffusivity, of the material. In highly interconnected material, Ar+ bombardment may seal pores, restricting O2 diffusion into the film and reducing damage compared to VUV/O2 alone. The effects of vacuum beam exposures are shown to be comparable to plasma exposures under 'plasma cure' (no energetic ion bombardment) and some rf-biased conditions. Using Fourier-transform infrared (FTIR) spectroscopy and mercury probe measurements, we show that VUV/O2 exposure causes loss of carbon, resulting in a hydrophilic, damaged layer that is susceptible to H2O absorption, which leads to an increased dielectric constant. These results suggest that both VUV photons and high-energy ions can play important roles in the generation of plasma-induced damage.

[1] Jinnai B, Nozawa T, Samukawa S 2008 *J.Vac. Sci. Technol.* B **26** 1926.

[2] Uchida S *et al.* 2008 *J. Appl. Phys.* **103** 073303

11:00am **PS-MoM9 Oxygen Containing Photoresist Ashing Chemistries with Less Damage to Low-k Films**, ***R. Gupta****, N. Stafford, C. Dussarrat, V. Omarjee*, Air Liquide

Oxygen-based plasma has been traditionally used for ashing patterned photoresist on low dielectric SiCOH (low-k) thin films. During the ashing process, energetic plasma species remove carbon (or CH3 group) from the exposed regions of the low-k film causing an increase in the dielectric constant of the film. The modified low-k film is also susceptible to water absorption which leads to higher dielectric constant and a degraded performance of the patterned device structure (such as collapsing and loss of critical dimensions) [1,2]. Moreover, higher porosity films will be required in future to achieve even lower dielectric constant and these films will be even more susceptible to plasma damage. Therefore, there was a need for new ashing chemistries to reduce the level of damage to the porous low-k film. A systematic study was performed with mixtures of O2 and selected molecules such as the standard CO2, CH4 or newly thought ashing chemistries. The ashing performance of the selected gas mixtures was compared with pure O2 for a similar thickness of resist removal. In order to highlight the chemistry effects of gas mixtures, the ashing was performed in similar conditions (i.e. RF power, temperature and pressure) as used for pure O2using a CCP RIE chamber.

A parametric study completed with pure O2 indicates that an increase in RF power and pressure generally leads to an increase in low-k damage. However, flow rate change with constant pressure did not show significant modification in damage characteristics. Damage to low-k film is improved by using gas mixture of the new chemistries and O2. The Hg-probe dielectric measurements reveal a least increase in dielectric constant with this mixture. Dilute Hydrofluoric (HF) acid tests also reveal the higher etch resistance of low-k films ashed with this mixture. Auger/XPS depth profile metrology is used to obtain elemental profiles of the damaged low-k films. In addition, residual gas analyzer data is being reviewed to understand better the etch gas chemistry to correlate to the damaging behavior of selected chemistries.

References:

Lee et al., Thin Solid Films, 517, (2009)

Zhou et al. AVS 2009. http://www.avsusergroups.org/pag_pdfs/2009_6zhou.pdf .

11:20am **PS-MoM10 Ultra-low k Integration Challenges and Plasma Etch Solutions For 22nm Node**, ***Y. Zhou***, *Z. Cui, J. Pender, S. Nemani, M. Naik*, Applied Materials Inc.

Higher porosity and new film chemistry are required to drive down k value of porous ultra low k (ULK) dielectrics integrated in advanced BEOL stacks. The challenge of integrating ULK dielectrics is compounded by shrinking dimensions. Taking a tri-layer resist via-first-trench-last integration scheme as an example, as the technology nodes progress, lower k value dielectrics are more prone to ashing damage. The resulting damaged layer accounts for a larger percentage of remaining film, resulting in higher integrated k value. Therefore, ashing improvement achieved for earlier nodes is not sufficient for the 22nm node. A particular ULK integration challenge is via to line spacing. The tight pitches at 22nm leave little tolerance for enlargement of the via size and shape. Previously acceptable levels of profile bowing can now directly lead to shorting. In this work, the challenges of ashing damage and via profile bowing are examined with a via first trench last integration scheme. It is identified that ashing is responsible for the majority of via profile bowing, and the key to reducing via bowing and ashing damage is to improve the ashing selectivity of organic mask to dielectrics. Different approaches are taken to improve ashing selectivity, including the traditional ashing chemistry/plasma optimization and a new pre-ash dielectric passivation scheme. These optimizations have significantly improved both physical and electrical performance.

11:40am **PS-MoM11 Highly Selective Etching of SiOCH over SiC Films by Dual Frequency CCP with DC Bias Superimposed to Upper Electrode**, ***T. Yamaguchi,*** *K. Takeda,* Nagoya University, Japan, *C. Koshimizu,* Tokyo Electron AT Limited, Japan, *H. Kondo, K. Ishikawa, M. Sekine, M. Hori*, Nagoya University, Japan

The dual frequency capacitively coupled plasma (CCP) with negative DC bias superimposed to the upper electrode has been proposed to realize high performance etching technologies. Denpoh *et al.* have discussed a mechanism under the DC bias superimposition that secondary electrons generated at the upper electrode transport through a bulk Ar plasma to the counter electrode. Kawamura *et al.* have also discussed about effects of the secondary electrons and a characteristic of the superimposed DC/RF sheath. Since the fluorocarbon (CF) etching plasma with the DC bias has not ever analyzed, we have measured various parameters and discuss the effect of the DC bias on the selective etching of SiOCH over SiC.

We used a CCP reactor for 300 mm wafer. VHF (60 MHz) power and DC bias were simultaneously applied to the upper electrode. RF (13.56 MHz) power was applied to the lower electrode where the samples were placed for etching experiments. A mixture gas of Ar, N_2 and C_4F_8 introduced with flow rates of 800, 100, and 10 sccm, respectively. Pressure was kept at 5.3 Pa.

Bulk plasma parameters such as electron density and CFx densities were measured when the DC bias changed. The electron density was 1.3×10^{11} cm^{-3} without the DC bias. In contrast, with the bias of -1200V, that gained up to 2.1×10^{11} cm^{-3}. This increase can be interpreted that positive ions accelerated by the DC bias bombarded the upper electrode with higher energy and then generated and supply more secondary electrons to the bulk plasma.

Notably, CF_2 radical density was decreased from 2.5 to 1.5×10^{13} cm^{-3} with the DC bias. It is well known that the bulk density depends on the surface loss probability, α, of the CF_2 radical. The α gained by dangling bonds creation by the ion bombardments. As the result, we believed that more fluorine-rich compounds in bulk plasma were lost by the adsorption and reaction on the reactive surfaces. In fact, with the DC bias of -1200V, SiOCH/SiC selectivity was improved significantly to 68 from 5.5without the DC biasing. This improvement was mainly brought by the etch rate decreasing SiC from 18.5 to 1.3 nm/min while the etch rate of the SiOCH film was maintained almost constant.

Surface analysis results showed that CF polymerized layer was not grew thicker on the SiOCH by such chemical reactions as C + O → CO, C + N + H → HCN. However, in the SiC case, a polymerized layer was relatively thicker because removal reactions were suppressed by lack of F-rich compound. Consequently, the highly selective etching for SiOCH/SiC films was achieved by differentiating the polymerized layer formation.

Advanced Surface Engineering
Room: Cimmaron - Session SE+PS-MoM

Atmospheric Pressure Plasmas
Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE+PS-MoM1 Plasmajet Atmospheric Pressure Plasma: Effects of H2 Addition in N2 Main Plasma Gas on the Optical and Electrical Plasma Characteristics and on Si-based Film Composition**, ***D. Debrabandere***, *X. Vanden Eynde,* CRM (Centre for Research in Metallurgy), Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

Si-based coatings were deposited with a cold plasma jet (Plasmabrush® PB1 from Reinhausen Plasma) at atmospheric pressure with nitrogen as main plasma gas and hexamethyldisilazane (HMDSN) as precursor. Effects of hydrogen addition on the plasma characteristics and the coating composition have been evidenced with optical emission spectroscopy (OES), power measurements and XPS in-depth analyses of deposited coatings. The evolution of the nitrogen line (at 315.9 nm) intensity with the applied voltage (ranging from 3.0 kV to 4.5 kV) has a sigmoid shape for the pure nitrogen plasma but it is quite linear with hydrogen addition (up to 3%). Based on OES spectra, the presence of the NH specie in the nitrogen-hydrogen plasmas has been evidenced (around 336.0 nm) but not in the pure nitrogen plasma. The power measured showed the same evolution with the applied voltage as the nitrogen line optical emission intensity: sigmoid shape for the pure nitrogen plasma and straight line for the nitrogen-hydrogen mixture. Although the plasma power is in similar range for both gases (except for applied voltages from 3.2 to 3.6 kV), the nitrogen concentrations in the films as evidenced by XPS were lower with the nitrogen-hydrogen plasma than with the pure nitrogen plasma indicating a chemical effect of the presence of hydrogen in the plasma.

Acknowledgements

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8:40am **SE+PS-MoM2 Plasma Polymerization at Atmospheric Pressure: an Environmental Friendly Approach to Synthesize (ultra)hydrophobic, Biocompatible, Hybrid, Barrier or Ion – Exchange Coatings**, *D. Merche, J. Hubert, F. Dabeux, B. Nisol, A. Batan, N. Vandencasteele,* ***F. Reniers***, Université Libre de Bruxelles, Belgium

Plasma treatments are widely used in various applications, such as surface modification (etching, grafting, cross-linking…), cleaning, pollutant removal, and thin films deposition. They are advantageous since they have a low energy cost, they do not release toxic organic solvents into the environment, they are easy to control (the main parameters to control the plasma are the current, voltage, frequency and the gas pressure and composition) and they can be run at room temperature. The plasma polymerization technologies at atmospheric pressure were developed more recently. They allow avoiding expensive vacuum set up, and can be easily implemented in a continuous production line. Two major configurations were used for the deposits: direct (in a DBD system) and remote mode (atmospheric torch). The synthesis conditions (in one step, starting from a liquid precursor, and using an atmospheric pressure plasma) of various types of coatings will be presented and discussed :PEG[1] and PTFE-like coatings [2] (for biocompatible coatings), multifunctional hybrid coatings for barrier properties [3] ; sulfonated polystyrene membranes for fuel cell applications [4,5] . The chemical structures of the various coatings were studied by XPS, FTIR and SIMS spectrometry. Correlations between the chemical structure and composition of the coatings and the plasma parameters were established.

[1] B. Nisol, C. Poleunis, P. Bertrand, F. Reniers, “Poly(ethylene glycol) Films Deposited by Atmospheric Pressure Plasma Liquid Deposition and Atmospheric Pressure Plasma-Enhanced Chemical Vapour Deposition : Process, Chemical Composition Analysis and Biocompatibility”, Plasma processes and polymers, (2010) under press

[2] N. Vandencasteele, O. Bury, F. Reniers "Process to deposit a fluorinated layer on a support", WO/2009/030763

[3] A. Batan, F. Brusciotti, I. De Graeve, J. Vereecken, M. Wenkin, M. Piens, J.J. Pireaux, F. Reniers and H. Terryn, "Comparison between wet deposition and plasma deposition of silane coatings on aluminium", Progress in Organic Coatings , (2010) under press

[4] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, “Synthesis of PS thin films by means of an atmospheric pressure plasma torch and a dielectric barrier discharge”, IEEE trans. on plasma science, 37 (2009), 951-960.

[5] Delphine Merche, Julie Hubert, Claude Poleunis, Patrick Bertrand, Philippe De Keyzer, François Reniers "Synthesis of sulfonated PS films using a Dielectric Barrier Discharge high pressure plasma" plasma processes and polymers, submitted

9:00am **SE+PS-MoM3 Surface Treatment of Energy Conversion Device Components by Cold Atmospheric Plasma**, ***L. Bardos***, *H. Barankova*, Uppsala University, Sweden

Advantage of virtually unlimited substrate sizes makes the cold atmospheric plasma very attractive for treatments of surfaces e.g., for improving the lifetime and performances of renewable energy conversion systems. Samples of fiberglass-reinforced vinylester with a vinylester based gelcoat from windmill turbine blades and steel sheets used for ocean buoys in the linear wave energy converters have been treated by the Fused Hollow Cathode (FHC) and Hybrid Hollow Electrode Activated Discharge (H-HEAD) atmospheric plasma, generated in Ar, Ne and a mixture of air with water. The resulting surface energy has been examined by contact angle measurements. Turbine blade surface becomes hydrophilic after the treatment, sticking of the water droplets is reduced and the surface dries fast after rain, snow or icing. An increased surface tension after plasma treatment of steel relaxes within about 60 min. However, the SEM observations of paint-steel interfaces after an immediate application of the protective paint on treated surfaces have confirmed a considerable improvement of the paint adhesion that can provide better corrosion resistance and lifetime of buoys. Results of tests under different plasma parameters are presented and discussed.

9:20am **SE+PS-MoM4 Smooth and Self-Similar SiO_2-like Layers on Polymers Synthesized using Dielectric Barrier Discharge Assisted CVD at Atmospheric Pressure**, ***P. Antony Premkumar***, *S.A. Starostin,* Eindhoven University of Technology, Netherlands, *H. de Vries,* FUJIFILM Manufacturing Europe BV, Netherlands, *M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

High quality inorganic oxide thin films applied over polymers are of significant technological interest in the field of optics, vapour barrier coatings, microelectronics, flat panel displays and protective coatings. The layers prepared by PECVD at atmospheric pressure (AP-PECVD) is considered as a promising technology due to its economical and technological advantages. Despite these benefits, the major challenge of this coating technology is the usually reported poor film quality which arises mainly due to the intrinsic instabilities of the plasma as well as from the complex reactions of the deposition process.

In this investigation, we demonstrate the remarkable SiO_x film properties synthesized using AP-PECVD in a roll-to-roll configuration [1]. The depositions were performed, in He free gas mixtures, using uniform glow-like dielectric barrier discharge as the electrical sources to assist CVD at atmospheric pressure. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N_2 or air) employed, the films are smooth, both in short and long range length scales, and of near stoichiometric silica with very low carbon content (<2%). Detailed AFM morphology description and surface statistical analysis on SiO_2 dynamics showed that no dynamical film roughening in growth front and lateral directions are observed and the synthesized layers (~ 350 nm) follow the topology of the substrate, mimicking its surface texture characteristics. The value of the roughness exponent (α), close to 1, determined from the height-height correlation function analysis, indicates a self-similar scaling of the SiO_2-like film morphology with the polymer substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O_2 and H_2O permeation.

[1] P. Antony Premkumar, S.A. Starostin, M. Creatore, H. de Vries, R.M.J. Paffen, P.M. Koenraad, M.C.M. van de Sanden, *Plasma. Proc. Polym*. (2010) In Press

9:40am **SE+PS-MoM5 Atmospheric-pressure Plasma Activation of Silicon and Glass Surfaces for Low-Temperature Direct Bonding**, ***C.-P. Klages***, *M. Eichler,* Fraunhofer Institute for Surface Engineering and Thin Films (IST), Germany, *B. Michel*, Technische Universität Braunschweig / Institut für Oberflächentechnik (IOT), Germany **INVITED**

Low-temperature direct bonding of silicon wafers has been industrially established for several years now. To achieve a lowered annealing temperature required for sufficient bond strength from about 1000 °C to a few 100 °C only, low-pressure plasma treatment came into use more than 20 years ago. As shown at Fraunhofer IST more recently, also plasma activation at 1 bar is capable of reducing required annealing temperatures to around 100 °C while still achieving bond energies 2 to 3 times higher compared to RCA-cleaned reference wafer pairs.

Many questions concerning the key effects, responsible for lowering the required annealing temperature, are still under investigation, especially for the attractive atmospheric-pressure method. At IOT and IST, the effects of dielectric barrier discharge (DBD) treatments performed under a wide range of conditions at 1 bar pressure on the properties of native or thermal SiO_2 layer on silicon wafers and on the achieved bond strength have been investigated in the recent years. The presentation will give an overview of the results from these investigations which were obtained using several surface analytical methods.

Recently, main interest has shifted from silicon to other materials and to alternative atmospheric-pressure plasma processes. With special gases used for the plasma activation, an increased bonding strength is also achievable for borosilicate glass bonding. However, while the mechanism of bonding enhancement in case of native oxide layers on Si can clearly be attributed to a surprisingly rapid growth of a porous oxide film, a convincing explanation for the effects achieved with glasses is still missing.

A common attribute of surface activation by DBD and low-pressure plasmas is a direct access of the plasma to the surface. By contrast, corona discharge makes use of the inhomogeneity of the electric field near a needle tip. Plasma zone and wafer are spatially separated and the electric field stress at the wafer surface is greatly reduced. Promising results of corona discharge treatment as an activation method for low-temperature wafer bonding have been obtained, indicating that relatively stable charged species play an important role. On the other hand, excimer UV radiation was virtually ineffective.

New insights into the kinetics of silanol condensation were also made possible by continuous measurements of the bonding strength *in situ* during annealing. Results of these studies show that the bond strength increase can be attributed to the expansion of bonded micro regions instead of statistical formation of siloxane bridges between the wafers.

10:40am **SE+PS-MoM8 Atmospheric Pressure Microcavity Plasma Arrays for Spatial Surface Modification**, *R.D. Short,* ***S. Al-Bataineh***, *E. Szili, C. Priest, Ph. Gruner,* University of South Australia, *E. Anglin,* Flinders University, Australia, *H.J. Griesser,* University of South Australia, *N. Voelcker,* Flinders University, Australia, *D. Steele*, University of South Australia

Microplasmas, a rapidly growing technology, are normally operated at or near atmospheric pressure with dimensions ranging from microns to millimetres. [1] We are developing this technology for surface modification without using a physical mask or additional processing steps to increase the versatility and cost-effectiveness of the technology. Micropatterning of various chemistries and biomolecules is seen as vital to the successful development of new and emerging technologies, such as microfluidics and high throughput cell screening tools. [1, 2] In this presentation, the fabrication process of microcavity plasma array devices will be introduced, followed by a demonstration of the utility of these devices for generating specially well-controlled micron-scale surface treatment and polymer deposition. Two issues regarding the utility of these devices for localised surface modification were investigated: 1) Can these devices be used to modify a surface with micron-scale features without having the substrate pressed against the array? 2) Can this be achieved with control over diffusion of the plasma reactive components? We explored this through XPS imaging and small spot analysis, which gave insights into the surface chemistry of the micron-scale modified areas. Finally, we demonstrate the utility of microcavity plasma array surface engineering in the development of biological cell arrays.

1. Iza, F., et al., *Microplasmas: Sources, particle kinetics, and biomedical applications.* Plasma Processes and Polymers,

2008. 5(4): p. 322-344.

2. Klages, C.-P., et al., *Microplasma-Based Treatment of Inner Surfaces in Microfluidic Devices.* Contributions to Plasma

Physics, 2007. 47(1-2): p. 49-56.

11:00am **SE+PS-MoM9 Electrical Characterization of Dielectric Barrier Discharges of Various Electrode Geometries**, ***V. Rodriguez-Santiago***, *J.K. Hirvonen, B.E. Stein,* U.S. Army Research Laboratory, *D.R. Boris, S.G. Walton,* U.S. Naval Research Laboratory, *D.D. Pappas*, U.S. Army Research Laboratory

The increased use of atmospheric-pressure plasmas for the surface modification of materials has drawn particular interest in understanding the basic phenomena underlying dielectric barrier discharges (DBDs). One of the main advantages of using DBDs is the generation of cold, non-equilibrium plasma at atmospheric pressure conditions without the need of vacuum equipment. A typical DBD setup consists of one or both electrodes covered with a dielectric material with a sufficiently high applied voltage to ignite the plasma. The plasma can be either filamentary or spatially uniform

depending on parameters such as dielectric and electrode material, interelectrode gap, carrier and reactive gas mixture, and the type of applied voltage among others. Another important aspect is the geometry of the electrode assembly, which will determine the electric field configuration and thus influence the discharge characteristics.

In this study, we investigate the electrical characteristics of He and He-O_2 dielectric barrier discharges using a pulsed, sinusoidal signal in the kHz frequency range with a (1-10) kV peak-to-peak amplitude. Full characterization of the plasma will be carried out using rod, sheet and planar electrode assemblies, while materials of various dielectric constants such as mica, quartz and polyethylene will be employed. Voltage, current and power distributions will be analyzed aiming to identify the optimal electrode geometries and dielectric materials needed to produce uniform and large scale plasmas for materials processing.

11:20am **SE+PS-MoM10 ICP Atmospheric Plasma Torch with Saddle-like Antennas for Yttrium Oxide Nanocoating**, ***Y. Glukhoy**, H. Schiesser*, American Advanced Ion Beam Inc.

ICP atmospheric plasma torch is the most powerful electrode-less heat generating system with relatively small dimensions and a reasonable consumption of power and gases. It serves as an universal tool for nanocoating of surfaces where the gaseous, liquid as well as powder precursors can be used. A total melting, evaporation and plasma chemical reaction of precursor can be achieved with torches that provide a sufficient residential time a high temperature plasma fluid. But a conventional torches are supplied by a coil inductor pinching this fluid due to an axial magnetic filed. In result, a high temperature area is reduced and a sufficient part of precursor is converted in dust. In order to broaden and lengthen this area for a sufficient increasing of a residential time the inductor has been replaced with two saddle-like ICP antennas with the different frequencies, i.e. 27.12 and 13.56 MHz. Each antenna comprises two or more spiral coils in a mirror position and in series or parallel connection. These coils are distributed with an angular uniformity and envelop a quartz tube of a plasma reactor. Such an non-axisymmetric design allows generation of a transversal RF field directed normally to axis of this reactor. But a plasma fluid is fixed on the axis due to buoyancy in the centrifugal force field created by a swirling injection of a discharge and sheath gases. However, the temperature gradient and a pressure drop caused by a cold carrier gas injected with a high velocity axially into a plasma bulk generate turbulence disrupting and distorting the plasma fluid. In result, a heat transfer from plasma to the wall is increased, becomes non-uniform and creates a hot spot melting the quartz wall. Mechanisms of the non-axisymmetric coupling, torch generation, contribution of different factors in distortion of the plasma fluid and method elimination of the hot spot have been investigated. In addition, we will discuss recent effort to extend applications such a torch in different areas including fabrication of yttrium oxide anti-corrosive nanocoating of focusing rings used in plasma etching processes in semiconductor industry.

1. Y.Glukhoy, I. Ivanov RF Atmospheric Plasma Systems for Nanopowder Production and Deposition of Nanocrystallines. AVS 53rd International Symposium, San Francisco, California, November , 2006 CA, USA .

2. Y.Glukhoy. Saddle-like ICP Antenna for RF Atmospheric Plasma Processes. AVS 56th International Symposium, San Jose, California, November , 2009 CA, USA .

Plasma Science and Technology
Room: Aztec - Session PS1-MoA

Advanced FEOL / Gate Etching I
Moderator: A. Metz, TEL Technology Center America

2:00pm **PS1-MoA1 Reduction of Plasma Induced Silicon-Recess During Gate Over-Etch Using Synchronous Pulsed Plasmas**, ***M. Darnon***, *C. Petit-Etienne, F. Boullard, E. Pargon, L. Vallier, G. Cunge, P. Bodart, M. Haass,* CNRS-LTM, France*, S. Banna, T. Lill*, Applied Materials Inc.

With the downscaling of CMOS devices in semiconductor industry, very thin layers (<1.5nm) are now introduced in transistor gate stacks. Integrating such thin layers presents tremendous challenges, particularly for the etch processes which have to be stopped selectively without inducing damage to the thin materials below. For instance, bulk silicon may be oxidized during the gate over-etch step through the thin gate oxide, which leads to silicon recess during the subsequent wet cleanings. In this contribution, we will precise the mechanisms of silicon oxidation through the thin gate oxide, and we will propose solutions to minimize this phenomenon by pulsing the plasma.

The experiments are performed on a state of the art 300mm AdvantEdge™ etch reactor equipped with the Pulsync™ system which provides full plasma pulsing capabilities at frequencies between 100 Hz and 20 kHz, with duty cycles between 10 and 90 %. In-situ spectroscopic ellipsometry is used to determine etch rates on thick silicon oxide and polysilicon layers, and to investigate plasma induced oxidation through a 2.5nm thin silicon oxide coated on bulk silicon. An angle resolved XPS system connected to the reactor allows quasi in-situ surface characterizations.

We show that an infinite selectivity of polysilicon over SiO_2 is obtained using an $HBr/O_2/Ar$ gate over etch process on thick layers. However, when a thin layer of silicon oxide is exposed to the same process, the thin oxide layer thickness increases with the plasma exposure time. This thickness increase is related to plasma induced oxidation through the thin gate oxide. XPS analysis show that a $Si\text{-}Br_x$ interface layer builds up between SiO_2 and Si, and that some bromine is incorporated in the oxide. This suggests that bromine implantation through the SiO_2 layer may generate a path in the oxide layer facilitating the oxygen and water diffusion (from the plasma or from the atmosphere) down to the SiO_2/Si interface

We show that plasma induced oxidation can be minimized by using synchronous pulsed plasmas. This way, we move from a highly dissociated plasma to a highly recombined plasma. As a consequence, radicals are larger and less prone to diffuse, and ions are molecular rather than atomic, which decreases the net energy of their components. Hence, bromine incorporation is highly limited and no $Si\text{-}Br_x$ interface layer is created, which minimizes silicon oxidation through the thin gate oxide.

These experiments clarify the mechanisms of plasma induced oxidation through the thin gate oxide, and show the promises of synchronous pulsed plasmas to reduce silicon recess.

2:20pm **PS1-MoA2 Control of Si Damage in Dry Etch Beyond 22nm Technology Node**, ***J. Guha***, *C. Lee, V. Vahedi*, Lam Research Corporation

The continuous shrinking of CMOS device node have put stringent requirement on reducing plasma induced damage and under layer film loss during dry etch. It is always almost the case that when a film is etched in a plasma the under layer film sustains some extent of damage and in some cases this film is etched leading to recess. Up until now this was within the noise to some extent, but beyond 22nm technology node this will be critical in defining device performance. Si roughness and recess during FEOL etch (like gate and spacer) results in degradation of device performance; like shift in threshold voltage, high leakage current leading to increased power consumption. These are some of the roadblocks in achieving high device performance at high packing density. Therefore, it is desirable to attain infinite selectivity between the film that is intended to be etched and its underlying film such that the under-layer film is damage free. In many cases strategies to control Si damage leads to tradeoffs like tapered profile which is not acceptable. This talk will discuss some of the issues in controlling Si damage in FEOL applications and some interesting results.

2:40pm **PS1-MoA3 Structural and Electrical Characterization of HBr/O_2 Plasma Damage to Si Substrate**, ***M. Fukasawa,*** Sony Corporation, Japan*, Y. Nakakubo, A. Matsuda, Y. Takao, K. Eriguchi, K. Ono,* Kyoto University, Japan*, M. Minami, F. Uesawa,* Sony Corporation*, T. Tatsumi*, Sony Corporation, Japan

Suppression of Si substrate damage caused by energetic ion bombardment is one of the most critical issues in advanced devices. Si substrate damage during gate electrode etching causes the “Si recess” structure, which is reported to degrade device performance. In previous work, we developed a bilayer model (surface oxide/dislocated Si) of the damaged layer and studied monitoring methods. In this paper, we have investigated the damage generation by plasma exposure and the removal of damage by wet treatment. We have also studied the impact of the damage on electrical performance. A dual frequency (60/13.56 MHz) CCP reactor was used in this study. A SiO_2 layer (1.7 nm) was formed on the Si substrate and exposed to HBr/O_2, H_2, and O_2 plasma. The pressure and Vpp were kept constant at 60 mTorr and 420 V. Diluted HF (100:1) was used to perform a wet treatment. The Si substrate damage was analyzed by spectroscopic ellipsometry (SE), HRBS, and TEM. In the SE analysis, data was fitted using a four-layer model (ambient/SiO_2/dislocated Si/substrate). Dislocated Si was modeled as a mixing of SiO_2 and polysilicon. C-V characteristics were measured with a mercury probe system. HBr/O_2 plasma generates a thicker surface oxide layer than O_2 plasma. The root cause of the thick oxide layer is enhanced diffusion of oxygen in the dislocated Si layer generated by deep penetration of H^+ from the plasma. The thickness of the oxide layer (T_{ox}) increased monotonically with increased exposure time (t) and reached about 10 nm at 600 s. The T_{ox} was found to depend on $t^{1/2}$, which is a so-called parabolic relationship (diffusion-controlled oxidation) in the Deal-Grove model. The T_{ox} and the thickness of the underlying dislocated Si layer (T_d) were compared by SE, HRBS, and TEM. The results were quite consistent across all analyses. The T_{ox} and T_d after dHF treatment were also analyzed. The surface SiO_2 was completely removed and the upper part of the dislocated Si was also eliminated (generation of Si recess). As the remaining dislocated Si was mainly caused by H^+ ion penetration, the C-V characteristics for H_2 plasma-exposed samples were analyzed. A negative bias voltage shift was observed, which implies the generation of positive charge trapping in the interface between the surface oxide and the dislocated Si layer. To minimize the Si damage during gate etching, it is necessary to control the H^+ penetration depth within the thickness of the thin gate oxide by controlling the IEDF precisely. Thus, quantitative control of the IEDF, precise monitoring of surface structure, and understanding the effects on device performances are indispensable for creating advanced devices.

3:40pm **PS1-MoA6 FEOL Etch Challenges for Beyond 2x Technology Node: What does it mean for Energy Consumption?**, ***C. Lee***, *M. Davis, V. Vahedi*, Lam Research Corporation **INVITED**

Energy reduction has become an emerging trend for semiconductor equipment manufacturing; as the technology evolves, demands for higher throughput on the etching of high aspect ratio structures (as driven by DRAM and NAND devices) have placed more demands on the amount of RF power required. A direct consequence of this is more energy is required, both to drive the RF generators and to provide the cooling necessary in order to remove heat generated. This talk will provide an overview on direct energy resource usage, such as power, water, thermal load, process gas usage, and what role does each of these play in the beyond 2x technology node.

4:20pm **PS1-MoA8 Advanced Gate Patterning of Novel Multi-Gated Devices for 15nm Node and Beyond**, ***S.U. Engelmann***, *Y. Zhang, M.A. Guillorn, S. Bangsaruntip, N.C. Fuller, W.S. Graham, E.M. Sikorski*, IBM T.J. Watson Research Center

To continue scaling CMOS devices at the traditional pace following Moore ’s law, Short Channel Effects (SCE) are the major issues limiting the use of planar device geometries for future technology nodes. Alternative device integration schemes are currently being tested to test the impact on SCE and extend technology nodes even further. The device candidates that are currently being tested include planar devices, FinFETs, Trigates and Nanowires (gate all around device). The gate formation on these advanced, multi-gated devices imposes completely new challenges on the plasma etch conditions, which translates to the demand to control the plasma process in a second (and a third) dimension. E-beam lithography has been proven to be a very valuable tool to explore plasma processing at device sizes unattainable by state-of the art optical lithography. We have demonstrated the fabrication of gates above a Fin of varying dimensions of gate and fin for SRAM cells down to 0.025um^2. Significant challenges for this

integration lie in the gate as well as the spacer formation, while maintaining the Si fin that has no hardmask to prevent plasma damage. While maintaining a vertical gate profile, no Silicon loss was observed on the Si Fin. A more significant challenge is the spacer formation, where Nitride needs to be removed from the fin sidewall, while maintaining it on the gate sidewall to prevent device shorts. An even higher degree of process control is needed in the fabrication of nanowire or gate all around devices. Maintaining a vertical gate profile while not damaging or destroying nanowires of diameters less than 5nm is critical. A gate recess process was employed to release the nanowire structures. A highly selective spacer rie process was developed to yield nanowires down to 3nm in diameter.

4:40pm **PS1-MoA9 Plasma Etching Challenges for Patterning Advanced Gate Stacks for 22nm Node and Beyond**, ***Y. Zhang****, S.U. Engelmann, Q. Yang, R.M. Martin, E.A. Joseph, M.A. Guillorn, E.M. Sikorski, W.S. Graham, B.N. To, N.C. Fuller*, IBM T.J. Watson Research Center

There are increasingly more challenges facing by patterning advanced gate stacks due to continuously scaling of CMOS device dimensions to 22 nm node and beyond. The major causes are from the following: (1) new materials being introduced for advanced gate stacks to enable continuously scaling of T_{inv}; (2) continuously shrinking of pitch and higher density; (3) complex gate patterning integration schemes, such as double or multiply exposures and double or multiply etching with multiply layer mask schemes due to the delay of EUVL; (4) 3D active area and gate structures, such as finFET, tri-gate, Si nanowire (SiNW) FET, etc.; and (5) move to the deep-nanometer regime, such as ETSOI with < 5nm Si channel. The 3D structures with the combination of novel materials and sub-50nm pitches for gate stacks impost unique challenges and demands on plasma etch process technology and news integration schemes and plasma etch tooling innovations. To meet all the requirements of target pitches, device feature profile, line edge roughness (LER) or line width roughness (LWR), and device performance/functionality, Different and unconventional approaches have to be introduced in plasma etching processing to fabricate 3D fins/active area, gates and spacers, particularly with the use of metal/high-k dielectric gate stack materials. Recent results illustrating some of these etching challenges including the progresses developed aiming on improving 3D profiles and achieving increased control of LER/LWR for fin, gate and spacer structures will be presented.

5:00pm **PS1-MoA10 High Selectivity SiN Etching with Low Damage by RLSA Microwave Plasma**, ***M. Inoue****, M. Sasaki, Y. Ohsawa*, Tokyo Electron, LTD., Japan

New materials such as High-K/Metal Gate and three-dimensional structures such as Tri-Gate have been introduced at the 22nm node and beyond. In addition, high selectivity and reduced Plasma Induced Damage (ex. Charge up damage and Si crystal damage, etc.) are required of the etching process. Especially, Fin Spacer of Tri-Gate is required high selectivity to thin oxide. RLSA (Radial Line Slot Antenna) microwave plasma has several features that overcome these new challenges. The characteristics of RLSA plasmas include high density, low electron temperatures and low plasma potential. In addition, Radical/ion ratio is higher than conventional plasma source. These characteristics enable highly selective etching with decreased Plasma Induced Damage on the wafer surface. A high SiN/SiO selectivity process has been achieved due to the features of RLSA plasma and low bias (low Vpp) conditions.

We have recently developed a high selective SiN/Si etching process under low bias conditions. It is thought that the mechanism for this etch includes minimum oxidation (native oxide level) of the Si surface to SiO, creating a highly selective etch similar to the SiN/SiO process that was previously developed.

5:20pm **PS1-MoA11 Impact of Plasma and Annealing Treatments on 193nm Photoresist Line Width Roughness and Profile**, ***L. Azarnouche****,* STMicroelectronics, France*, E. Pargon, K. Menguelti, M. Fouchier,* Ltm - Umr 5129 Cnrs, France*, R. Tiron,* CEA-LETI-MINATEC, France*, P. Gouraud, C. Verove,* STMicroelectronics, France*, O. Joubert*, Ltm - Umr 5129 Cnrs, France

As the Critical Dimension (CD) of gate transistors scales down to the nanometer range, line width roughness (LWR) becomes a serious issue, which directly impacts the electrical performance of CMOS devices. It has previously been shown that the photoresist (PR) sidewall roughness present after lithography (6nm, 3σ) is transferred during the subsequent plasma etching processes into the gate, resulting in a final LWR far above the ITRS requirements for the 32nm technological node (1.7nm, 3σ). The key to decrease the final gate LWR is to minimize the photoresist LWR before the plasma etching steps involved in the gate patterning process. The best and simplest way is to expose the photoresist patterns to plasma treatments prior to gate patterning. Indeed, it was observed that Vacuum Ultra Violet (VUV) light emitted by plasmas plays a key role in the photoresist LWR decrease. In the present study, we have used CD-SEM and CD-AFM techniques to investigate the impact of plasma treatment on the photoresist LWR and profiles. Several plasmas (HBr, Ar, He, H_2) emitting strongly in the VUV region (100-200nm) have been investigated. LiF windows placed between the plasma and the photoresist patterns have been used to evaluate the role of the plasma VUV light only on the LWR evolution. The role of the substrate temperature has also been studied. Many characterization techniques have been used to characterize the physico-chemical modifications of photoresist films exposed to the same plasma treatments (Multiple Internal Reflection infrared spectroscopy (MIR), Raman, gas chromatography (GC)).

The results obtained indicate that all plasma treatments lead to a LWR decrease. We have observed that for all plasma investigated, VUV light only seems to induce a slight reflow of the resist which is probably correlated with the LWR decrease. On the other hand, in HBr and Ar plasmas, resist patterns remain square indicating that no reflow occurs. Heating resist patterns up to 200°C without plasma exposure also leads to a LWR decrease, resist reflow being only observed above 200°C . All treatments generate the cleavage of the side groups (lactone group for plasma treatment and protecting group for annealing treatment) and the decrease of the glass transition temperature which is potentially correlated to the LWR decrease. GC analysis also reveals that under Ar and HBr plasma exposure, cleaved side groups can be trapped in the resist polymer matrix because of the presence of a denser surface layer. This dense layer could prevent the resist reflow leading in final to the square profiles observed in HBr plasmas.

Plasma Science and Technology
Room: Galisteo - Session PS2-MoA

Atmospheric Plasma Processing and Micro Plasmas
Moderator: A. Rousseau, Ecole Polytechnique, France

2:20pm **PS2-MoA2 High Current Diffuse Dielectric Barrier Discharge in Atmospheric Pressure Air for Thin Silica-Like Film Deposition**, ***S.A. Starostin****,* Eindhoven University of Technology, Netherlands*, P. Antony Premkumar,* Materials Innovation Institute (m2i), Netherlands*, M. Creatore,* Eindhoven University of Technology, Netherlands*, H. de Vries,* FUJIFILM Manufacturing Europe BV, Netherlands*, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

The dielectric barrier discharge (DBD) is recognized as a promising tool of thin films deposition on various substrates at atmospheric pressure. Emerging applications including encapsulation of flexible solar cells and flexible displays require large scale low costs production of transparent uniform dense layers with low level of surface defects. Unfortunately the common operational mode of the atmospheric pressure DBD is filamentary, resulting in strong spatial non-uniformity of plasma chemistry and affecting the quality of the deposited films. Sustaining of the filament-free non-thermal plasma over the large area substrate at atmospheric pressure remains a challenging task especially considering the discharge in ambient air [1].

In present contribution the diffuse dielectric barrier discharge in atmospheric pressure air was applied for the thin film deposition on polymeric web in industrially relevant roll-to-roll configuration. The silica-like film deposition was performed using the admixture of hexamethyldisiloxane precursor to air flow. Discharge diagnostics was realized by means of fast ICCD imaging; time resolved optical emission spectroscopy and electrical characteristics analysis. ICCD discharge imaging confirms plasma uniformity in a microsecond time scale, while at nanosecond time scale shows fast propagating lateral ionization waves. Morphology and composition analyses, performed by means of AFM, ATR-FTIR and XPS methods, indicate that the process results in ultra-smooth films (roughness comparable to initial substrate roughness) and shows the possibility to synthesize carbon-free layers.

[1] S.A. Starostin, P. Antony Premkumar, H. de Vries, R.M.J. Paffen, M. Creatore, and M.C.M. van de Sanden *Appl. Phys. Lett*. **96**, 061502 (2010)

2:40pm **PS2-MoA3 Microscale, Atmospheric-Pressure Plasmas for Nanomaterials Synthesis**, ***R.M. Sankaran***, Case Western Reserve University **INVITED**

Large-scale, low-pressure plasmas play an essential role in the manufacturing of integrated circuits that are now ubiquitous in consumer electronics. In recent years, new challenges have arisen for these top-down approaches to materials processing. Future electronic devices will incorporate nanoscale materials such as nanoparticles, carbon nanotubes,

and silicon nanowires that cannot be fabricated by current plasma technology because of limitations associated with photolithography. In addition, emerging applications in sensors, energy, and medicine require materials that must be prepared from the "bottom-up". The aim of our research is to develop a new class of plasmas, termed "microplasmas", for nanomaterials synthesis.

Microscale plasmas or microplasmas are a special class of electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their unique scaling, microplasmas operate stably at atmospheric pressure and contain large concentrations of energetic electrons (1-10 eV). These properties are attractive for a range of nanomaterials applications. Vapor-phase metal-organic precursors can be dissociated at ambient conditions (i.e. room temperature and atmospheric pressure) to homogeneously nucleate metal[1] and alloyed[2] nanoparticles. The formation of metal nanoparticles in the gas phase allows direct introduction of these materials as catalysts for carbon nanotube and silicon nanowire growth[3]. Recently, we have also coupled microplasmas with liquids or polymeric films to nucleate nanoparticles from metal ions[4]. In this talk, I will discuss these topics in detail, highlighting the advantages of microplasma-based systems for the synthesis of well-defined nanomaterials.

1. W-H. Chiang and R. M. Sankaran, "Microplasma synthesis of metal nanoparticles for gas-phase studies of catalyzed carbon nanotube growth," Appl. Phys. Lett., Vol. 91, 121503 (2007).

2. W-H. Chiang and R. M. Sankaran, "Synergistic effects in bimetallic nanoparticles for low temperature carbon nanotube growth," Adv. Mater., Vol. 20, 4857 (2008).

3. W-H. Chiang and R. M. Sankaran, "Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni Fe nanoparticles," Nat. Mater., Vol. 8, 882 (2009).

4. C. Richmonds and R. M. Sankaran, "Plasma-liquid electrochemistry: Rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations," Appl. Phys. Lett., Vol. 93, 131501 (2008).

3:40pm **PS2-MoA6 Micro-discharge Plasma using Silicon Platform**, ***M.K. Kulsreshath***, *T. Dufour, P. Lefaucheux, O. Aubry, S. Dozias, P. Ranson,* CNRS/Université D'Orleans, France*, J.-B. Lee, M.J. Goeckner, L.J. Overzet,* University of Texas, Dallas*, R. Dussart*, CNRS/Université D'Orleans, France

Micro-discharges can be produced in a variety of different configurations and using a variety of different technologies. The properties of these micro-discharges have been examined with increasing interest during the past decade. There has also been intense interest in new fabrication techniques for the production of micro-discharges. In this paper we present the fabrication technology used to make micro-discharge "reactors" on a silicon (Si) substrate along with selected plasma properties. For the fabrication of these reactors we have used 4" Si wafers and standard cleanroom facilities. The fabrication technology used is compatible with standard CMOS device fabrication and the micro-discharge reactors fabricated can be used to produce either DC or AC discharges. The micro-discharges operate well at high-pressure. They were given planar cathodes and ring-shaped anodes separated by a SiO_2 dielectric with a thickness of approximately 5-6 µm rather than the much more common ~100 µm. The micro-discharge reactors can consist of either a single hole or multiple holes and we have built devices with holes from 25 to 150 microns in diameter. The micro-discharge measurements were obtained for inert gas, DC plasmas between 100 and 1000 Torr. Although we used only a single ballast resistor, many hole micro-discharges were obtained because the cathode surface area of each micro-discharge was limited. This also acts to limit the discharge power. In addition, we will report on current leakage and parasitic sparks during high pressure operation. Finally, we discuss the spread of the micro-discharge over the anode and cathode surfaces as well as the life time of the micro-discharge reactors.

4:00pm **PS2-MoA7 Electron Current Extraction from rf Micro-Dielectric Barrier Discharges**, ***J.-C. Wang***, University of Michigan, Ann Arbor*, N. Leoni, O. Gila,* Hewlett Packard Research Labs*, M.J. Kushner*, University of Michigan, Ann Arbor

Micro dielectric barrier discharges (mDBD's) consist of micro-plasma devices (10-100 µm diameter) in which the electrodes are fully or partially covered by dielectrics, and operate at atmospheric pressure driven with radio frequency (rf) wave forms. After the plasma is generated charging of the dielectric terminates the discharge. At atmospheric pressure, particularly in attaching gases, the plasma formation and decay times can be as short as a few to tens of ns whereas the rf period may be tens to hundreds of ns. So the micro-plasma may need to be re-ignited with each discharge pulse. In certain applications, it may be desirable to extract electron current out of the mDBD plasma, which necessitates a third electrode. As a result, the physical structure of mDBD and the electron emitting properties are important to its operation. In this presentation, we will discuss the properties of mDBD's sustained in atmospheric pressure N2 and air using results from a two-dimensional plasma simulation. The micro-DBD's are sandwich structures with an opening of ten-of-microns excited with rf voltage waveforms of up to 25 MHz up to 0.5 mm away. The model, nonPDPSIM, solves Poisson's equation and transport equations for charge species and electron energy conservation equation for electron temperature. Rate coefficients and transport coefficients are obtained from local solutions of Boltzmann's equation for the electron energy distribution. Radiation transport is addressed using a Green's function approach. We find that following avalanche by electron impact ionization in the mDBD cavity, the plasma can be expelled from the mDBD's cavity towards the collection electrode during the part of the rf cycle when the collection electrode appears anodic. This extraction can be enhanced by biasing the extraction electrode. At lower frequencies, the plasma needs to be reformed every cycle. Long lived neutral species facilitate the generating of plasma by production of UV photons that continuously seed secondary electrons at surfaces until the potential is favorable to re-ignite plasma. The amount of extracted charge per pulse is not a strong function of rf frequency for values up to 25 MHz, but is sensitive to the dielectric constant of the barrier. For applied voltages of up to 2-3 kV, electric field emission appears not to play an important role.

4:20pm **PS2-MoA8 Ignition and Extinction of a Micro Hollow Cathode Discharge Operating in DC Regime**, ***R. Dussart****, M.K. Kulsreshath, T. Dufour,* CNRS/Université D'Orleans, France*, L.J. Overzet,* University of Texas at Dallas*, P. Lefaucheux, T. Tillocher, O. Aubry, S. Dozias, P. Ranson,* CNRS/Université D'Orleans, France*, M.J. Goeckner,* University of Texas at Dallas*, J.-B. Lee*, University of Texas, Dallas

Microdischarges have gained the interest of the plasma community for the 15 past years. Among them, Micro Hollow cathode Discharges (MHCDs) have the very interesting property to operate at atmospheric pressure in a stable non thermal regime. We have studied the ignition and extinction of such microdischarges. Our samples are made in alumina, covered by a 5 µm thick Nickel layer on both sides and drilled by a laser process. We made experiments in helium and argon at a pressure between 100 and 1000 Torr. To initiate the plasma, we increase the discharge voltage linearly and slowly (20 sec) until the voltage breakdown was reached. During the microplasma ignition, a high current pulse as high as several tens of microamps appeared before a stable and constant lower value was obtained. We will compare these current pulses to those obtained in the so-called self pulsing regime. We will also show electrical and optical measurements carried out to characterize the phenomenon. Finally, we will show the discharge current and voltage temporal evolution at the very last moments of the microplasma, just before its extinction. The physical mechanism of the ignition and extinction will be discussed to explain the measured waveforms.

4:40pm **PS2-MoA9 Characterization and Applications of Three Different Configured Atmospheric Pressure Plasma Sources**, ***Z. Ouyang****, V. Surla, S. Jung, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The Center for Plasma-Material Interactions (CPMI) at the University of Illinois at Urbana-Champaign has developed large-scale microwave-induced atmospheric plasma sources for use in various manufacturing applications. The microwave source employed has a working frequency at 2.45 GHz, and a maximum input power of 6 kW. Plasma sources of three different configurations have been developed in order to tailor the plasma configuration to various specific applications. A cold plasma torch head has the ability to generate an atmospheric plasma with a temperature range from room temperature (20°C) to more than 1,000 °C. A thermal plasma torch has been developed such that the temperature range extends to 2,000 °C. A linear line source suitable for production line integration has the ability to sustain a 20-centimeter long atmospheric plasma. Various gas compositions (He, Ar, N_2 and O_2) are used to reveal the functionalizations of different radicals and particles. OES system has been used to analyze critical characteristics such as electron density (n_e~$10^{14}$$cm^{-3}$) and temperature ($T_e$~1eV), plasma temperature (T_g~300-2,000K) under different operating conditions and results of material processing correlated to those measurements so that a selectable and repeatable material process can be obtained. Hydrophilicity tests on polymer substrates reveal that the "cold" atmospheric plasma has the ability to modify the surface energy within seconds of exposure at a relatively low flux of incident particles, without deforming bulk material substrates; while the "thermal" atmospheric plasma is used to assist in Nd:YAG laser ablation (f=100Hz, P_{av} = 2.0W at 266 nm, 12.5W at 532nm, and 32.5W at 1064nm) of metal or ceramic materials, to provide a means to deposit high quality contamination free films on substrate with better lamination at a relatively higher deposition rate (~5,000 nm/min) in comparison to traditional PVD methods.

5:00pm **PS2-MoA10 Study of Atmospheric Pressure Plasma Jets: The Influences of Ambient Air and the Application on ZnO Thin Film Deposition**, ***Y.J. Yang***, *Y.W. Hsu, Y. Lin, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This presentation includes the diagnostic studies of an atmospheric pressure plasma jet (APPJ) and the use of this plasma jet to perform ZnO thin film deposition. The APPJ under investigation is sustained by a pulsed power supply with a repetitive power frequency up to 25 kHz using N_2 or O_2 as the plasma gas. The assessment of how the ambient air influences the plasma characteristics and how it can effectively be minimized are the focus of the diagnostic work. To minimize the ambient air influence, the exit of the jet is shielded with a glass tube with the inside diameter ranging from 3 to 5 cm . The exit of the tube is covered by a metal plate and leaving a gap of 0.5 to 3 mm. When the N_2 plasma is used, the visible jet length is much longer with such an arrangement. The effective area within which the jet is treated increases by more than a factor of two, as confirmed by the contact angle measurement made on the treated glass surface. In O_2 plasmas, the intensity of atomic oxygen emission (777.4 nm) increases by more than one order of magnitude with the presence of the glass tube. When photoresist is etched using this oxygen plasma jet, the jet with the presence of the glass tube shows a increase in the etching rate by more than 50 % than the case without the presence of glass tube.

The use of this APPJ to perform ZnO thin film deposition is studied as the second part of this presentation. ZnO thin films are deposited on a silicon wafer by spraying nebulized zinc-containing salt solutions, namely $ZnCl_2$ and $Zn(NO_3)_2$, into the downstream of the plasma jet. Preliminary studies show that by using N_2 plasmas, a better quality film can be obtained comparing with using O_2 plasmas. The film quality is found to be sensitive to the plasma conditions. With properly adjusted process parameters, dense and smooth films can be deposited with a rate higher than 75 nm/min. Improvement of the electrical conductivity and the study of the photoluminescence properties of the film are currently underway.

5:20pm **PS2-MoA11 Atmospheric-Pressure Microplasma-Jet Modified Polystyrene Surfaces as Substrates for Epithelial Cell Growth**, ***J.-S. Oh***, *J.W. Bradley, K.G. Doherty, C.M. Sheridan, R.L. Williams, A. Bowfield, P. Unsworth, P. Weightman*, The University of Liverpool, UK

Non-thermal atmospheric pressure plasma jets (APPJs) have recently been the subject of much interest as an alternative to low-pressure plasma treatment since they are relatively simple to construct, and have the advantages that expensive vacuum equipment and high grade gases are not needed. APPJs have potentially numerous applications such areas such as deposition, surface modification and particularly, in biomedicine, sterilization and wound treatment. Here we focus on developing micro-plasma jet technology based on capillary dielectric barrier (DBD) discharges for the localized surface modification of polystyrene (PS) as a substrate for biomaterial processing. The micro-capillaries have an internal diameter of 280 μm and an outer diameter of 330 μm. The surface modification is spatially investigated by dynamic water contact angle (WCA) measurement with about ~0.2 μL water droplets. The results show that the WCA of untreated PS is 90° reducing to angles between 30° and 20° for exposure times between a few seconds and several minutes. The treated areas have typically radial extensions of several millimeters varying with discharge voltage, excitation frequency, gas flow rate and capillary-substrate distance. The modified surface properties will be discussed in more detail with focus on X-ray photoelectron spectroscopy measurements of the surface chemistry and the relationship to epithelial cell culture growth and proliferation.

Advanced Surface Engineering
Room: Cimmaron - Session SE+PS-MoA

Pulsed Plasmas in Surface Engineering
Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-MoA1 2010 AVS Peter Mark Award Lecture - High Power Impulse Magnetron Sputtering (HIPIMS) - Fundamentals and Applications**, ***A.P. Ehiasarian****, Sheffield Hallam University, UK **INVITED**

High power impulse magnetron sputtering (HIPIMS) is one of the youngest magnetron sputtering technologies. It provides new parameter space and new level of control of deposition parameters which are unattainable by conventional sputtering or cathodic arc evaporation technologies.

HIPIMS utilises a short (impulse) gas discharge with duration of ~100 μs and duty cycles of <1% allowing it to access high peak power densities of 3000 Wcm^{-2} at voltages of several hundred volts and current density of 1-4 Acm^{-2}. Within each HIPIMS pulse the discharge is ignited through a hot electron ionisation wave and then develops into a cold metal plasma. The properties of the target material such as sputter yield, secondary electron emission coefficient, atomic mass and ionisation potential determine the power dissipated in the discharge, the density of plasma and the transport from the target to the substrate. The lifetime of both gas and metal ions spans over several milliseconds after the pulse often extending to the next pulse, thus creating a constant bombardment of ions at the substrate.

The degree of metal ionisation is controlled by the peak power density dissipated at the target and reaches 50% for Ti and 70% for Ta. The high metal ionization fraction of the HIPIMS technology has been utilised in applications for metalizing high-aspect vias with depth-to-width ratio of 30:1 achieving 10% bottom coverage for Ti, Ta and Cu films. The technology has been upscaled to a production cycle for through-silicon via (TSV) interconnects on 200 mm wafers.

HIPIMS pretreatment can implant metals and rare earths in substrates whilst maintaining the crystalline character, promoting local epitaxial growth over large lateral areas and excellent adhesion. This enables the introduction of oxidation- and corrosion- barriers at the coating-substrate interface.

Reactive sputtering in Ar and N_2 atmosphere in HIPIMS are characterised with a strong dissociation of the nitrogen molecule. In conditions of high power density, the N^{1+} : N_2^+ ratio and Ti^{1+}:Ti^0 ratio can exceed 1 thus promoting a fully dense intercolumnar boundaries in TiN films and increase their hardness. A preferred growth orientation of (200) is observed even without substrate biasing.

Nanoscale multilayer (superlattice) structured coatings based on CrAlYN/CrN have been grown with very low waviness and strongly improved density. These coatings provide excellent oxidation resistance and reduced fatigue deficit of aerospace turbine blades.

Nanocomposite coatings based on CrAlSiN were also deposited by HIPIMS for applications in high-temperature oxidation protection. Closer packing and reduced misorientation of nanocrystals as well as increased size of nanoclusters in which they are grouped are crucial mechanisms crucial in enhancing the film hardness.

The technology is finding new applications in the deposition of $Cu(InGa)Se_2$ in industrial photovoltaic cell coaters where a 3% improvement in efficiency over conventional sputtering has been achieved.

2:40pm **SE+PS-MoA3 Influence of Plasma Conditions on the Properties of Hafnium and Titanium Films Deposited using HIPIMS**, ***A.N. Reed***, Air Force Research Laboratory, *M.A. Lange*, Air Force Research Laboratory/Universal Technology Corp., *J.G. Jones, C. Muratore, J.J. Gengler, A.A. Voevodin*, Air Force Research Laboratory

The orientation of a film can have a significant effect on its physical properties, for example the thermal conductivity of hexagonal materials. There has been a significant amount of work in the area of controlling the microstructure of films using deposition parameters. High power impulse magnetron sputtering, HIPIMS, is a PVD technique that produces a sputtered flux with a higher ion content than conventional DC magnetron sputtering. The ionization fraction of material upon the substrate permits some control of the film characteristics. In this study films were grown at pressures ranging from 5-30 mTorr, and pulse duration from 20-200μs. The resulting films exhibited pressure dependent deposition rates as well as changing crystalline structure based on pulse duration. Energy resolved mass spectrometry and optical emission spectroscopy allowed correlation of ion energy distributions to deposition rates. Material characterization techniques, such as XRD, XPS, and SEM, have been used to correlate film structure to processing conditions for hafnium, titanium, and their nitrides. Time-domain thermal reflectance was used to measure the films' thermal conductivities. Differences in these values were related to the film microstructure.

3:40pm **SE+PS-MoA6 High Power Impulse Magnetron Sputtering for the Growth of Functional Amorphous and Nanocrystalline Films**, ***K. Sarakinos***, *A. Aijaz, M. Samuelsson, U. Issaksson, U. Helmersson*, Linköping University, Sweden **INVITED**

Growth of films by condensation from the vapor phase frequently proceeds far from thermodynamic equilibrium giving rise to metastable configurations with unique attributes which are largely determined by the energy of the film forming species. One way of transferring energy to the growing film is via bombardment by ionized species which are present in plasma assisted physical vapor deposition (PVD) techniques. High power impulse magnetron sputtering (HiPIMS) is a novel plasma assisted PVD technique in which large fluxes of energetic ions are made available at the growing film. This is achieved by applying the power to the target in short

* Peter Mark Memorial Award Winner

unipolar pulses of low duty cycle (<10%) and frequency (<10 kHz). This mode of operation results in the generation of ultra dense plasmas (electron densities 10^{18}-10^{19} m^{-3}) and a subsequent high degree of ionization for both gas atoms and sputtered material. HiPIMS has been extensively used for the deposition of polycrystalline elemental and compounds films facilitating control over their microstructure, phase composition, optical, mechanical and electrical properties. In the present talk the use of HiPIMS for the deposition of amorphous and nanocrystalline carbon and metal nitride based films is demonstrated. Discharges are generated using a variety of experimental parameters with respect to the pulse width, pulsing frequency, composition and pressure of the gas atmosphere. Time-averaged and time-resolved plasma diagnostics reveal that the variation of the above mentioned process parameters allows for control over the flux, the energy and the nature of the bombarding ionized species. Growth of films at those conditions enables to tune their bonding properties, their microstructure and their crystallinity and through this tailor important functional attributes such as their mechanical performance and high temperature stability.

4:20pm **SE+PS-MoA8 New Development in Modulated Pulse Power Sputtering of Aluminum Oxide, Aluminum Nitride and Carbon Films***,*
R. Chistyakov*,* Zond Inc*, B. Abraham*, Zpulser LLC

Modulated pulse power (MPP) sputtering is a versatile high power pulse magnetron sputtering technique in which there can be multiple voltage steps within a pulse. In this study, multiple voltage steps have high amplitude voltage oscillations. It was found that at certain level of voltage oscillations amplitude and frequency it is possible to sustain near arc free discharge in reactive gas environment. A special plasma generator with adjustable voltage oscillations amplitude and frequency was developed. The maximum output voltage is 1400 V. Aluminum oxide and aluminum nitride films have been reactively deposited with new approach in near arc free mode. The deposition rate, film structure, orientation, and mechanical properties were analyzed and measured, and the results of the film property measurements will be presented. Carbon films were sputtered with high average and peak power. It was found that with particular voltage pulse shapes there is no cones formation on the target surface during the deposition

Plasma Science and Technology
Room: Aztec - Session PS1-TuM

Advanced FEOL Etching II
Moderator: A. Agarwal, Applied Materials Inc.

8:20am **PS1-TuM2 Sidewall Polymer Management of sub 20nm Shallow Isolation Trench (STI) Etch via Pulsed Plasma**, ***X. Hua**, X. Ji, J. He, J.H. Choi, A. Khan*, Applied Materials Inc.

The thickness of sidewall polymer accumulated on feature is typically a few nanometers during plasma etching. How to manage this thin polymer layer becomes critical to successful pattern transfer by plasma etch, because it equals >10% of the actual feature size as semiconductor devices are aggressively scaled down below 20nm. The impact of this thin layer on conductance of species in the features is not negligible any more when feature size is shrunk below 20nm, especially in high aspect ratio applications. To make minimum depth loadings, i.e. intro cell/micro loadings, and ideal feature profiles are extremely challenging and strongly dependent on how we manage this sidewall polymer. In this wok, we will discuss how we can utilize pulsed plasmas to manage this polymer layer. Since the residence times of typical plasma etch conditions are in order of ms~s and the period of pulsed plasma is ~ms, species has extra time to move into or out of the feature when it is the off cycle, as compared conventional plasma sources of continuous wave mode. This unique property of pulsed plasma leads to 1) thinner polymer coverage (less redeposition, radicals moving out of the feature) or 2) thicker polymer accumulation (more deposition, radicals moving into the feature from the gas phase), depending on plasma conditions. Better introcell/ micro loadings, more rounded/less pinch off trench bottom are demonstrated by using low duty cycle (<60%) pulsed plasmas than continuous wave plasmas. The influence of duty cycles/frequency of the pulsed plasmas on feature profile, depth loading was investigated in details. In synchronized pulsed plasmas, continuous tapered trench profile is demonstrated with no pinchoff bottom. With optimized duty cycle ratio between source and bias powers, microloading is achieved below 5% of etch depth (>300nm). Pulsed plasma has shown enormous advantage over conventional continuous wave plasma source to control the pattern transfer of future semiconductor fabrications.

8:40am **PS1-TuM3 Feature Scale Model of Shallow Trench Isolation (STI) Etch in HBr Plasma and Comparison with Experiments**, ***S. Sriraman**, T. Panagopoulos, A. Paterson, H. Singh, V. Vahedi*, Lam Research Corporation

Continued scaling in the semiconductor industry provides new challenges for critical etch applications in front-end logic and memory devices. As device sizes shrink, control of Shallow Trench Isolation (STI) features to create active area islands become more important. Typical logic STI performance metrics for a 300mm wafer include trench angle, trench depth and iso-dense depth loading and their corresponding within-wafer uniformity. In addition to these metrics, memory STI application includes a challenging requirement for intra-cell depth loading that arises due to within-feature variation of the space critical dimensions (CD) in the dense feature array. These stringent profile control requirements are typically met by operating halogen-based Transformer Coupled Plasma (TCP™) in the mid-pressure operating regime.

This paper will discuss the semi-empirical feature scale model of STI etch in HBr plasma to address iso-dense and intra-cell trench depth loading for an etch stack representative of memory STI features. Plasma diagnostics and reactor-level models are implemented to characterize the HBr plasma produced in the TCP configuration process chamber. Kinetic parameters in the model are constrained by matching simulated feature profiles with those experimentally obtained at various process conditions that are a subset of the process space of interest. The feature scale model is quantitatively calibrated to the experimental profiles and validated for prediction within the process space. The validated profile simulator is used to identify reactor-level process knobs that minimize iso-dense and intra-cell depth loading. The advantages of calibrated process-specific profile simulation in enabling efficient exploration of parameter space during process development and future challenges facing STI trench depth etch will be discussed.

9:00am **PS1-TuM4 Synchronous Plasma Pulsing For Etch Applications**, ***M. Haass****, *M. Darnon, E. Pargon, C. Petit-Etienne, L. Vallier, P. Bodart, G. Cunge,* CNRS-LTM, France*, S. Banna, T. Lill,* Applied Materials Inc.*, O. Joubert*, CNRS-LTM, France

Plasma processes have been used for many years in the manufacturing of semiconductors. They have been so far the only technological solution to address the critical dimension control at the nanometer range imposed by the continuous downscaling of the CMOS devices dimensions.

However, the current etch processes are reaching their limits of controlling the etch selectivity and the critical dimensions at the atomic scale. In this study we investigate the potential of pulsed plasmas to further improve dry etching processes.

The experiments are carried out in a commercially available 300 mm AdvantEdgeTM tool from Applied Materials Inc. The inductively coupled plasma is sustained by two RF generators operating at 13.56 MHz, one to generate the plasma and the other mainly to polarize the wafer. These generators have been modified using the PulsyncTM system to allow pulsing at frequencies between 10 Hz and 20 kHz and duty cycles between 10 and 90 %. Even though a delay can be applied between the generators only the synchronous case is studied here. Several modifications of the plasma chamber were carried out in order to use advanced plasma diagnostics like in situ ellipsometry, UV absorption spectroscopy and mass spectroscopy. Furthermore an angle resolved XPS system is connected to the plasma chamber under vacuum allowing quasi in-situ analysis of the wafer surface after etching.

This article focuses on HBr/O2 plasmas dedicated to STI (Shallow Trench Isolation) etch processes. We demonstrate the ability of synchronously pulsed etch plasmas at different frequencies and duty cycles to modify the etched profiles strongly compared to the standard continuous case. Especially experiments carried out at a frequency of 1 kHz and a duty cycle of 20 % show a very distinct alteration. In this case, ellipsometry measurements indicate a sharp increase in time compensated etch rate (etch rate relative to the actual plasma ON time of the etch process). Additionally, the etched profiles show a strongly enhanced quality, in particular a high selectivity, uniformity and a minimization of the aspect ratio dependent etching phenomena. We demonstrate that these improvements are linked to the balance between plasma dissociation and recombination during the ON and OFF time of the pulsed plasma which can directly influence the composition of neutral and ion flux. This balance is controlled by the duty cycle rather than the pulsing frequency.

9:20am **PS1-TuM5 Characterization of Pulsed Plasma Etch Reactors with an Integrated Global Plasma-Feature Scale Model**, ***A. Balakrishna**, A. Agarwal, P. Stout, S. Rauf, K. Collins*, Applied Materials Inc.

Uniformity requirements (both etch rate and critical dimensions) for plasma etching of very small features (< 32 nm) are more stringent than ever. One particular challenge is minimizing feature distortion due to plasma induced damage. If the feature aspect ratio is high, via-like features in dielectric materials may physically twist/turn due to the stochastic nature of fluxes entering the feature as the size of the opening shrinks [1]. Limited quantity of polymer on the sidewalls exaggerates this feature distortion. Pulsed plasma operation is a promising approach to improve uniformity while reducing feature distortion [2]. Although pulsing of both capacitively and inductively coupled plasma (CCP/ICP) sources has been investigated before, novel pulsing schemes such as synchronously pulsed ICPs allow for expanded operating regime for damage-free etching of nanoscale features.

In this paper, pulsed and continuous plasma operation of an ICP reactor in electronegative gas mixtures will be discussed using results from a computational investigation. Earlier investigations [3] have linked a 2-dimensional plasma equipment model (HPEM) to a Monte Carlo feature profile model to assess the consequences of pulsed plasma operation on etching. Long computational times restricted the range of conditions that could be investigated, e.g. more complex chemistries or lower pulse frequencies. We have addressed this constraint by using a global plasma model (Zephyr) combined with analytical expressions for behavior in the sheath. The global plasma model is based on the methods described by Meeks et al [4]. This model calculates all the species (neutrals, ions and electrons) concentrations and their temperatures using time-dependent conservation equations, including both gas and surface reactions. The impact of different surface materials on plasma chemistry is also captured.

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* Coburn & Winters Student Award Finalist

The global plasma model is validated using more detailed 2-dimensional plasma modeling and experimental diagnostic results for simple chemistries (Ar, O_2). The validated model is then applied to pulsed plasmas of highly electronegative chemistries used for silicon etching (Cl_2 and HBr based). Results will be discussed for impact of pulse characteristics such as duty cycle, pulsing frequency, and phase lag between source and bias pulses on etching in an ICP chamber.

[1] M. Wang and M.J. Kushner, J. Appl. Phys. 107, 023308 (2010).

[2] S. Banna, et al., Trans. Plasma Sci. 37, 1730 (2009).

[3] A. Agarwal et al, J. Appl. Phys. 106, 103305 (2009).

[4] E. Meeks, H.K. Moffat, J.F. Grcar and R.J. Kee, SAND96-8218 (1996)

9:40am **PS1-TuM6 Atomic Layer Etching of Graphene using O_2 Radical and Ar Neutral Beam**, ***W.S. Lim***, *Y.Y. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Graphene is a two-dimensional hexagonal lattice of carbon atoms with the thickness of one or a few atomic layers. Due to its material stability and strength, absence of defects, and unique electronic band-structure, graphene holds considerable promise for a number of applications in nanoscale electronics, optoelectronics, and mechanics in addition to showing fundamental interest in condensed matter physics. Many potential applications, such as graphene-based high-speed field-effect transistors, require graphene to be patterned to the nanoscale and, in some cases, graphene needs to be etched precisely with atomic layer precision. However, through the conventional reactive ion etching, it is difficult to control the etch depth precisely due to the fluctuation of the etch process in addition to the damage to the graphene by the reactive ions.

In this study, to overcome the above problems, the atomic layer etching technique (ALET) has been applied in the etching of graphene, and the etch characteristics of graphene by ALET were investigated. For the adsorption gas, O_2 was used, and Ar neutral beam was used for the desorption of the adsorbed compound. For the few layer graphene deposited on the SiO_2 (300 nm)/ Si substrate, the monolayer etching condition of graphene was observed by supplying O_2 radical at a pressure higher than the critical pressure during the adsorption step and by supplying an Ar beam at a dose higher than the critical dose. Self-limited etching of graphene could be obtained using O_2 radical ALET.

10:40am **PS1-TuM9 Etching of Magnetic Stack for Development of Thermally-assisted Magnetic Access Random Memory**, ***J. Pereira***, *X. Mellhaoui*, LTM - UMR 5129 CNRS, France, *J. Shin*, Crocus Technology, France, *E. Pargon*, LTM - UMR 5129 CNRS, France, *J. Reid*, Crocus Technology, France, *O. Joubert*, LTM - UMR 5129 CNRS, France

Magnetoresistive Random Access Memories (MRAM) is of great interest since they combine the best characteristics of FLASH, SRAM and DRAM memories: non-volatility, low voltage operation, unlimited read and write endurance, fast read and write operation. One of the key parameters for M-RAM technology development is the etching of the Magnetic Tunnelling Junction (MTJ). Today, one of the main methods used for MRAM patterning is based on a pure sputtering dual Ion Beam Etching (IBE). However, IBE technique shows some technological limitations that increases the difficulty of MRAM device manufacturing. Indeed, it has low throughput and cannot be used to pattern very dense structures because of shadowing effects., The process can lead to magnetic materials redeposition on the pattern sidewalls that can short-circuit the dielectric tunnel junction. In this paper, we propose to develop plasma etching technologies to pattern complex stacks of MRAM devices as an alternative to IBE process, improving the manufacturability of MRAM devices.

The aim of this work is to investigate a full RIE process for the patterning of Thermally Assisted MRAM (TA-MRAM) dots in ICP reactors (Decoupled Plasma Source from AMAT).

We propose to investigate innovative plasma chemistries (without O_2, Cl_2 to avoid corrosion) to etch the magnetic materials composing the MTJ junction. CO/NH_3 plasmas assisted by temperature could be very promising plasma chemistries to form volatile metal-carbonyl etch by products and avoid redeposition on the pattern sidewalls.

Optical Emission spectroscopy and reflectometry is used to monitor the plasma process. The etching profile, critical dimensions (CD) and possible redeposition on sidewalls are analysed using Scanning Electron Microscopy (SEM), and Focused Ion Beam devices (FIB-SEM, FIB-TEM). The nature of non-volatile by-products re-deposition is studied using X-Ray Photoelectron Spectroscopy.

11:00am **PS1-TuM10 III-V Etch Challenges for Beyond 20nm Node**, ***U. Shah***, *B. Turkot, M. Radosavljevic, M. Shaw, S. Clendenning, B. Chu-Kung*, Intel Corp.

The scaling of CMOS transistors to 20nm and beyond may invoke utilization of materials that are far different in electrical and mechanical properties from conventional silicon. InGaAs, InP, GaAs are examples of such materials being considered for future device fabrication and as such will present numerous challenges for etch. These include balancing profile needs against stringent selectivity and scalability requirements to address the myriad of device needs at this node. Etch characterization of these materials using various processing chemistries (Cl2, CH4, H2), tool conditions (chuck temperature, power, bias, pressure) and tool types, as well as a variety of material stacks has been carried out using 3-4" wafers. GaAs and InGaAs etch rates of ~40-45A/s at high chuck temperature of 225 degrees are obtained for 30nm lines spaced at 1-50um. A linear relationship between etch rate and temperature is also observed with H2/Cl2 chemistry. Chuck temperature impact on trench/ line profiles is understood on the basis of volatility of the byproducts as well as on the nature of the resulting sidewall passivation. Data showing the difficulties in pitch scaling and controlling etch rates of stacked materials will also be discussed.

Plasma Science and Technology
Room: Galisteo - Session PS2-TuM

Plasma Diagnostics, Sensors and Control
Moderator: U. Czarnetzki, Ruhr-University Bochum, Germany

8:00am **PS2-TuM1 Wafer-level Plasma Parameters Measurements in a Multi-Frequency Capacitively Coupled Plasma Discharge**, ***L. Dorf***, *S. Rauf, J.A. Kenney, K. Bera, N. Misra, K. Collins*, Applied Materials Inc.

Two complications with wafer-level measurements in a capacitively coupled plasma (CCP) discharge are very high DC (~ -1kV) and radio-frequency (RF) (~2kV peak-to-peak) voltages of the substrate, and the lack of theoretical basis for interpretation of volt-ampere characteristics (VACs) of the probes inside the RF sheath. In this work, we present the diagnostic apparatus that measures ion current to the wafer, along with near-sheath plasma density (n_e) and electron temperature (T_e). Particle-in-cell (PIC) and fluid plasma simulations are used to help interpret collected VACs. Measurements are performed using a set of radially distributed planar double probes (DP). The electronic circuit located outside of the discharge chamber provides: (1) DC isolation and RF filtering of the high voltage, (2) biasing voltage to the probes, (3) switching between the probes, and (4) probe current measurements. Electrical signals are brought in and out of the chamber using a specially designed feed-through and a low-profile connection to the substrate. Results of wafer-based measurements performed in an Applied Materials CCP chamber at a variety of rf-frequencies (2, 13, 162 MHz), rf power levels (300 – 1000 W), neutral fill pressures (30 – 100 mT), chemistries (Ar, O2, Ar/CF_4), and magnetic field configurations are presented. At low frequency, pressure was found to have stronger effect on ion current and plasma density than that at intermediate and high frequencies; in all chemistries. The effect of mixing low and medium frequencies with the high frequency was found to be most pronounced at the periphery of the discharge. Magnetic field was confirmed to be a powerful knob for controlling radial uniformity of the discharge at all frequencies; namely, edge current and density tend to increase with application of the magnetic field. To interpret VACs, a 2-dimensional fluid plasma model was developed for the CCP chamber with a DC-biased pad on the substrate. This model was used to calculate current at the DC-biased pad versus applied DC voltage, i.e. single probe (SP) VAC. The SP VACs for a variety of discharge rf-voltages and neutral pressures were then used to derive the DP VACs, which were in turned analyzed using standard experimental techniques to obtain plasma parameters. Those were found to be in a good agreement with near-sheath plasma parameters calculated self-consistently by the fluid model. PIC simulations confirm the results of fluid simulations, but also highlight the highly non-equilibrium nature of electron energy distribution at the electrode.

8:20am **PS2-TuM2 In-situ Measurement of High-Frequency Current and Voltage in Etching Chambers**, ***S. Kobayashi***, *H. Hanawa, K. Ramaswamy, S. Rauf*, Applied Materials Inc.

A set of electrical probes have been developed to measure high-frequency current and voltage, close to electrode surfaces in inductive and capacitive etching chambers. Attenuating radio-frequency (RF) voltage probes are often used for voltage measurements in plasma chambers. However, at high frequencies over 50 MHz, the reading of RF voltage by these probes

strongly depends on how the grounding wire is connected to a posited earth point. On the other hand, a voltage probe of the capacitive divider-type provides the voltage reading defined by the direction of dominant electric field, resulting in physically meaningful data even over 100 MHz. The latter approach is therefore taken. Since this voltage probe is designed with a high input impedance, the 50 ohm cable of an arbitrary length can be connected so as to place its sensing part in a small space of a chamber. Our current probe design is based on the pick-up coil approach. However, this current probe is designed to remove contamination of electric field from current reading. After precise calibration, both the probes can be mounted at any surface of the plasma etching chamber.

The probes are firstly used to monitor the etching uniformity in a capacitive plasma discharger operated at 162 MHz. The experimental concept is based on the electrical control methodology proposed by Sobolewski et al. (1999). Due to the 162 MHz standing wave built up in the transmission part of the chamber, the interpretation of current and voltage measurements is not so straight-forward. However, the voltage probe, mounted close to the wafer position shows better correlation with etching uniformity compared with another commercialized voltage probe mounted at the exit of the RF match box.

In the second experiment, these electrical probes are used to monitor the phase difference between two floating electrode in a capacitive discharging etching chamber. This experiment is aimed at testing the approach suggested by Bera et al. (2008). While experiments on uniformity-control via RF-phase was reported in the literature of Sung et al. (2009), one problem with these experiments is that the phase shift was monitored in the pre-match position. Unless special care is taken to characterize the match state, the phase change controlled by the phase-shifter would not have provided precise information on phase between the two electrodes. In our experimental set-up, this issue will be overcome by monitoring voltages close to the electrode surfaces.

These preliminary experiments indicate that these high-frequency voltage/current probes have a broad range of in-situ applications in the future design of etching chambers.

8:40am **PS2-TuM3 The Determination of Energy Fluxes in Plasma Surface Interaction**, ***H. Kersten***, University of Kiel, Germany **INVITED**

Since the thermal conditions at substrate surfaces affect essentially the interaction of elementary processes during plasma treatment of solid surfaces (deposition, etching, modification), the experimental determination of the energy influx from plasma to substrate is of great importance.

The total energy influx can be measured by special calorimetric sensors (thermal probes). One method is based on the determination of the temporal slope of the substrate surface temperature in the course of the plasma process. The heating curve as well as the cooling curve (after switching-off) are fitted by suitable functions and the time derivatives at same environmental temperature are calculated. By knowing the calibrated heat capacity of the sensor the difference of the time derivatives yields the integral energy influx to the surface. Simultaneously, the electrical current to the substrate can be obtained and by variation of the sensors bias voltage the energetic contribution of charge carriers can be determined. By using thermal probes of different materials it is even possible to verify the effect of surface recombination, secondary electron emission and sputtering in respect to the energy balance of a substrate in plasma processing. By comparison of the experiments with model assumptions on the involved plasma-surface mechanisms the different energetic contributions to the total energy influx can be separated.

The method will be demonstrated for various process plasmas, e.g. magnetron sputtering (HiPIMS), asymmetric rf-discharge, ion beam source, and ECR afterglow.

9:20am **PS2-TuM5 Noninvasive Electrical Monitoring of Ion Current, Ion Energy, Electron Temperature, and Electron Yield**, ***M.A. Sobolewski***, National Institute of Standards and Technology

Traditional plasma diagnostic techniques that require inserting a probe into a plasma are not compatible with commercial plasma reactors and the manufacturing environment. In contrast, the radio-frequency (rf) current and voltage across a discharge can easily be measured outside the reactor, without perturbing the plasma or process. Furthermore, the waveforms of rf current and voltage contain information about process-relevant plasma properties. For example, one technique [1,2] has been developed which uses a numerical model of the plasma and its sheaths to analyze the waveforms and determine from them the total ion current and ion energy distributions. This method, however, assumes that the electron temperature is constant, and it neglects any emission of electrons from the electrode or substrate surfaces. To investigate errors arising from these assumptions, variations in electron temperature were measured by a Langmuir probe during fluorocarbon plasma etching of silicon dioxide films, and values for the yield of ion-induced and photon-induced electron emission were estimated. These results allow the resulting uncertainties in ion current and ion energy to be quantified. They also provide tests of how well the existing technique can be extended to also provide monitoring of electron temperature and emitted electron yield, in addition to ion current and ion energy.

[1] M. A. Sobolewski, J. Vac. Sci. Technol. A 24, 1892 (2006).

[2] M. A. Sobolewski, J. Appl. Phys. 95, 4593 (2004).

9:40am **PS2-TuM6 Controllable Electron Beam for Optical Emission Studies in Real-Time Process Plasmas**, ***G. Padron-Wells****, *P.L.S. Thamban*, University of Texas at Dallas, *J. Hosch*, Verity Instruments, *M.J. Goeckner*, University of Texas at Dallas

Process control in etch plasma systems are often achieved by optical emission spectroscopy (OES) signals. One such application is etch endpoint detection. In systems where plasma emissions are low, OES signals for process control cannot be employed. To address this problem, a versatile electron extraction method has been developed and used in conjunction with an OES diagnostic system to reliably measure changes in gas composition and emission cross sections for CF_4 plasma etch environments. An inductively coupled plasma source is employed to source electrons in an excitation region where optical emission measurements are conducted. Unique to this design is the control it offers to measure electron impact optical excitation of gas phase species. Cross section response for Argon emission lines with respect to electron beam energy correlates well with published data. Cross section behaviors for the strongest emission lines characterizing the CF_x molecular system are presented. Also, ability to detect 0.1% changes in feedstock gas chemical composition makes this design a highly sensitive end point detection system for analysis of semiconductor process chemistries. Work supported in part by NSF (Grant CBET- 0922962) and Verity Instruments.

10:40am **PS2-TuM9 A New Diagnostic Tool of Electron Energy Distribution Function in Capacitive Modes in High Frequency Plasmas**, *H. Shindo*, ***Y. Nakazaki***, Tokai University, Japan

A new diagnostic tool to measure Electron Energy Distribution Function (EEDF) by an emissive probe has been proposed[1] and applied to radio-frequency (RF) plasmas. In particular, the measurements are made in the capacitive mode which is occurred at the various frequencies of 2 to 60 MHz. It is generally difficult for a conventional probe method to measure EEDF in RF plasmas, because of the plasma potential fluctuation, particularly in the capacitive mode. On the contrary, one of the advantages of the present method is that the measurements are free from the high frequency potential fluctuation.

The method is based on measurement of the functional relationship between the floating potential change ΔV_F and the heating voltage V_H of emissive probe. If the Maxwellian plasma is concerned, the following equation can be obtained as a practical and useful formula.[1]

It is important to know that the value of ΔV_F contains information of electron energy distribution with several electron volt interval along the floating potential V_F, because ΔV_F is determined only by the current of plasma electrons with an energy interval.

In the experiments, the values of ΔV_F were measured in the Ar plasmas which were produced by a single-loop antenna[2] in the frequencies of 2 to 60 MHz and the gas pressures of 5 to 100 mTorr. The values of ΔV_F behave quite differently, depending on the frequency and the gas pressure, hence the plasma mode. It is found that the capacitive mode is appeared at the pressures below 20 mTorr at 2 MHz, 10 mTorr at 13 MHz, and at 60 MHz, the behavior of floating potential change ΔV_F is fairly complicated, hence non-Maxwellian plasma. In all capacitive modes, from the data set of ΔV_F and V_F, the electron energy probability function (EEPF) is calculated, and the EEPF thus obtained reveals a bi-Maxwellian with the two electron temperatures depending on the frequencies. For an example, the data set of ΔV_F and V_F at the pressures of 3 to 7 mTorr at 13 MHz revealed the high energy tail with the temperature of 3.0 to 5.0, while at 10 mTorr the EEPF showed a straight line, hence a Maxwellian. At 2 MHz, on the other hand, the capacitive mode was appeared even in higher RF power, but the two temperature mode was not so typical. It should be emphasized that the present diagnostic method becomes powerful in observation of the plasma mode transition in a variety of frequencies.

References:

[1] K.Kusaba and H.Shindo, Review of Scientific Instruments, **78**, 123503-1(2007).

[2] Y.Jinbo and H.Shindo, Applied Physics Express, **2**, 016001-1(2009).

* Coburn & Winters Student Award Finalist

11:00am **PS2-TuM10 Frequency Probe Measurements in Processing Plasmas**, ***D.R. Boris****,* NRL/NRC Postdoctoral Research Associate*, S.G. Walton,* Naval Research Laboratory*, M. Baraket,* NRL/NRC Postdoctoral Research Associate*, E.H. Lock, R.F. Fernsler*, Naval Research Laboratory

Plasma density measurements are an essential tool in understanding and controlling processing plasmas across a wide range of applications. Charge collection probes (Langmuir probes) are of limited utility in depositing plasmas, high pressure applications or in processes that require the use of reactive gases, as these environments result in unreliable data acquisition. Plasma frequency probes are an attractive alternative to Langmuir probes in such applications since they do not suffer significant performance degradation in these environments. Frequency probes are capable of measuring plasma density over a range of 10^8 to 10^{12} cm^{-3} and, it is possible to extract the plasma potential and electron temperature. This presentation details the use of plasma frequency probes, in a variety of different geometries, to measure plasma parameters in unique systems, such as plasma produced by electron beams, operating at higher pressures, or in reactive gases (O_2 and SF_6). Where possible these measurements are compared with Langmuir probe measurements for identical experimental parameters.

11:20am **PS2-TuM11 Probe Geometry Induced Electron Energy Distribution Function (EEDF) Distortion**, ***A.E. El Saghir*********, E.M. Martin, S.S. Shannon*, North Carolina State University

One of the most valuable plasma characteristics that can be obtained from a Langmuir probe is the Electron Energy Distribution Function (EEDF). This is carried out by subtracting the ion contribution of the probe current, the shape of the electron current for probe potentials lower than the plasma potential is used to reconstruct the EEDF. The integral relationship for electron current in the transition region of a single probe voltage-current characteristic has been previously derived for planar probe configurations[1]. The Druyvesteyn relation for obtaining EEDF's from Langmuir probes is derived based on a model that assumes that only an electron's energy component perpendicular to the electric field generated by the biased probe determines whether an electron is collected or deflected by the probe when operating with an electron retarding potential. Cylindrical and spherical probe geometries have an additional electron retarding mechanism not accounted for in the Druyvesteyn relation. This additional mechanism comes in the form of a centrifugal retarding potential whose strength is determined by the initial angular momentum when the electrons are far away from the probe. In this work, formulations for cylindrical and spherical geometries are presented. These integral relationships are used to demonstrate the impact of ignoring probe geometry in EEDF extraction and highlights distortion of EEDF's when these geometric considerations are not taken into account. Finally, by combining the integral formulation for cylindrical and spherical probes with the analytical findings of Hoskinson for a finite cylindrical probe[2], we present a study of the effect of finite length cylindrical probe geometries on EEDF solutions.

[1]Druyvesteyn M.J, Z. Phys.,vol. 64,1930, pp. 781-798.

[2]R. Hoskinson, and N. Hershkowitz, Plasma Sources Sci. Technol. vol. **15,** 2006,pp. 85-90.

This work is supported by the UNC General Assembly and a generous gift from Applied Materials

11:40am **PS2-TuM12 How Fast do Ions Fall Out of a Two Ion Species Plasma? Experimental Test of a New Theory**, ***N. Hershkowitz****, C.-S. Yip,* University of Wisconsin-Madison*, G. Severn*, University of San Diego

Recent experiments have shown that ions in weakly collisional plasmas containing two ion species of comparable densities nearly reach a common velocity at the sheath edge. A new theory suggests that collisional friction between the two ion species enhanced by two stream instability reduces the drift velocity of each ion species relative to each other near the sheath edge and finds that the difference in velocities at the sheath edge depends on the relative concentrations of the species. It is small when the concentrations are comparable and is large, with each species reaching its own Bohm velocity, when the relative concentration differences are large. To test these findings, ion drift velocities were measured near the near sheath edge in Argon-Xenon plasmas as a function of the concentration ratio using the laser-induced fluorescence technique. We show that the predictions are in good agreement with a revised version of the model. This is the first experimental test of the collisional friction model.

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* Coburn & Winters Student Award Finalist

Plasma Science and Technology
Room: Aztec - Session PS1-TuA

Advanced BEOL/Interconnect Etching II
Moderator: Y. Zhou, Applied Materials Inc.

2:00pm **PS1-TuA1 Reaction Mechanism and Profile Evolution for Cleaning and Sealing Porous Low-*k* Dielectrics using He/H_2 and Ar/NH_3 Plasmas**, ***J. Shoeb***, Iowa State University, *M.J. Kushner*, University of Michigan, Ann Arbor

Porous dielectric materials offer lower capacitances that reduce RC time delays in integrated circuits. Typical *low-k* materials include SiOCH – silicon dioxide with carbon groups, principally CH_3, lining the pores. Fluorocarbon plasmas are often used to etch *low-k* materials. These processes leave a fluorocarbon polymer on the *low-k* surface that must be removed. This is often done with oxygen containing plasmas. With porosities as high as 0.5, pores open to the surface and which are internally connected provide pathways for reactive species to enter into the porous network. Reactions during plasma cleaning of, for example, O atoms with the CH_x groups, can increase the *k* value of the material by removing C atoms. To maintain the low-*k* value, cleaning the CF_x polymer and sealing of the surface must be performed without significantly altering the SiOCH material properties, and not removing the CH_x groups. Plasma cleaning with He/H_2 mixtures is capable of removing these CF_x residues without harming the underlying low-*k* surface and can also strip off the hydrocarbone photoresist (PR) mask.

In this talk, we discuss results from modeling of the plasma cleaning and sealing of porous SiOCH in sequentially applied He/H_2 and Ar/NH_3 plasmas. The HPEM (Hybrid Plasma Equipment Module) was employed to obtain the ion energy and angle distributions of reactive fluxes from inductively coupled plasmas. These are used as input to the MCFPM (Monte Carlo Feature Profile Module) with which profiles of the low-*k* materials after the plasma exposures are predicted.

We found that hot hydrogen atoms can remove the CF_x polymer, generating mainly HF and fluorohydrocarbons such as CHF_2. These hot H-atoms can simultaneously remove H from the surface resident CH_3 groups thereby activating the SiOCH surface by creating C dangling bonds. He ions are also effective at breaking Si-O bonds creating dangling while also removing H-atoms from CH_3 group, both of which activate the SiOCH surface. Unlike O_2 plasma cleaning, the He/H_2 clean creates more reactive CH_x (x = 1,2) sites without significantly damaging the substrate. Following the He/H_2 plasma cleaning, NH_3 plasma treatment seals the pores by NH_x (x=1,2 and 3) species passivating previously produced dangling bonds, forming Si-N and C-N bonds.[1] Initial results indicate that combined He/H_2 and Ar/NH_3 plasma treatment of SiOCH with pores having radii of 0.8 nm can seal nearly 100% of the surface pores.

* Work supported by Semiconductor Research Corp.

[1] A. M. Urbanowicz, M. R. Baklanov, J. Heijlen, Y. Travaly, and A. Cockburn, Electrochem. Solid-State Lett. **10**, G76 (2007).

2:20pm **PS1-TuA2 Mechanism of Modification in Si-O-Si Structure in Porous SiOCH Low-k Films by H_2/N_2 Plasmas**, ***H. Yamamoto***, *K. Takeda, K. Ishikawa, H. Kondo, M. Sekine, M. Hori,* Nagoya University, Japan, *T. Imamura, H. Hayashi, I. Sakai, T. Ohiwa*, Toshiba Corporation, Japan

Introduction of porous low-dielectric-constant (low-*k*) materials such as porous (p-) SiOCH film, to the interlayer dielectric is important for improving performances of ULSI devices. The trench sidewall in the p-SiOCH film is known to suffer serious damage during the plasma processes. The *in-situ* evaluation is crucial for the clarification of damage generation mechanism because the damaged films are easily modified during air exposure. In this work, we have investigated the impact of ions, radicals and light from H_2/N_2 plasma and subsequent air exposure on Si-O-Si bond structure in the film using *in-situ* Fourier transform infrared reflection absorption spectroscopy. A 75-nm-thick p-SiOCH film was coated on 150-nm-thick Tungsten film deposited on Si substrate. A Si plate or an MgF_2 window which transmits light (greater than 115 nm in wavelength) was set 1 mm above or just on the film during the plasma exposure. Samples were placed on the lower electrode in a VHF-CCP etcher with (a) no plate for evaluating the interaction of ions, radicals, and light, (b) Si plate for evaluating the impact of radicals, (c) MgF_2 window for evaluating the effect of light and radicals, and (d) MgF_2 window with no space for evaluating the light effect. To investigate the Si-O-Si bond modification in the films, IR absorption signal in 985-1250 cm^{-1} were decomposed to three bands with peaks at 1035, 1065, and 1149 cm^{-1}, which correspond to the linear, network and cage structures, respectively. The change in the three peak area ratios were investigated after H_2/N_2 plasma and air exposures. The peak area ratio of the linear structure decreased and the ratio of network and cage structure increased after the H_2/N_2 plasma exposure in all samples. The ratio of linear structure decreased and the ratio of cage structure increased after the air exposure in all samples. In the case of sample (a), that was exposed to ions, radicals, and radiation, the amount of change in Si-O-Si structure was relatively smaller than the amount of decrease in Si-CH_3 bond. It was confirmed that a portion of Si-O-Si linear structure in the SiOCH film changed to network and cage structure with decrease in Si-CH_3 bond during the H_2/N_2 plasma exposure. Si-NH_2 bonds and dangling bonds formed by the plasma exposure reacted with water in the atmosphere and the Si-O-Si structure was modified with Si-OH bonds formation. Ion bombardment made the top surface shrink and the densified layer inhibited moisture uptake into the film during air exposure. This work was supported by Grant-in-Aid for Scientific Research (21・10187).

2:40pm **PS1-TuA3 Effect of UV-wavelength on Hardening Process of Porogen-containing and Porogen-free Ultra-low-*k* PECVD Glasses**, ***A.M. Urbanowicz***, *K. Vanstreels, P. Verdonck, E. Van Besien, Ch. Trompoukis, D. Shamiryan, S. De Gendt, M.R. Baklanov*, IMEC, Belgium

The ITRS scaling of ultra-large-scale integrated circuits requires mechanically robust materials with low *k*-value. Low-*k* materials recently used in the Cu/low-*k* integration scheme have *k*-values between 2.5 and 3.0. One of the limiting factors in further reduction of k-value is mechanical robustness, since major way to decrease *k*-value is increasing the material porosity. The PECVD low-*k* deposition of ultra low-*k* films uses a porogen-based approach. The matrix material is deposited by oxidation of alkylsilanes in a plasma-enhanced chemical vapor deposition (PECVD) process. The porogen molecules, usually cyclic hydrocarbons, are introduced into a SiOCH film by co-deposition with the matrix material. To create porosity, the porogen is removed from the films using UV-assisted-thermal curing.The porogen molecules are photo-dissociated by UV-light with the formation of volatile hydrocarbons and non-volatile carbon-rich residues (porogen residue) [1]. We have shown recently that SiOCH glasses with improved mechanical properties and ultra-low-*k* value could be obtained by controlled decomposition of the porogen molecules prior to the UV-hardening step [2]. The controlled removal of porogen can be performed by H2-based afterglow plasma treatment of PECVD film [1,2].

In this work we study the effect of narrow band 172 nm and broadband >200 nm UV-sources in the new curing scheme of the PECVD dielectrics. The data are compared with the PECVD films fabricated in the conventional UV-curing scheme. The effect of both 172 nm and >200 nm UV-sources is comparable for porogen-containing conventional PECVD films. However, the porogen-free films cured with 172 nm UV-source shows approximately twice as higher Young's modulus (YM) of 6.64 GPa (*k*100kHz ~ 2.2, 44% open porosity) than those cured with >200 nm UV with YM of 3.38 GPa (*k*100kHz ~ 2.0, 48% open porosity). The mechanical properties, optical properties 150 nm - 800 nm, dielectric constants at 100 kHZ and 4 GHz, porosities and pore size distributions, bonding structure are presented. The impact of porogen on optical characteristic and therefore on photochemical UV-hardening mechanism is discussed. The achieved mechanical properties are explained on a basis of the percolation of rigidity theory and random network concepts.

References

[1] A. M. Urbanowicz, K. Vanstreels, D. Shamiryan, S. De Gendt and M. Baklanov, Electrochem. Solid State Lett., 12, H292 (2009).

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3:00pm **PS1-TuA4 CF_3I for Low-k Etching: Overcoming Current Technology Limitations**, ***V. Omarjee***, American Air Liquide – Delaware Research and Technology Center, *A.G. Gildea, E. Eisenbraun,* The University at Albany-SUNY, *N. Stafford, F. Doniat, C. Dussarrat*, American Air Liquide – Delaware Research and Technology Center

Every technology node brings new processing challenges. The etching of low-k and ultra-low-k (k=2.4 and below) materials that are currently used in leading edge interconnects is very demanding. With a porosity varying from ~15 to 30%, the films are easily damaged during the various processing steps and it is easy to have undesired film modifications (physical defects,

collapse, impurity penetration, roughening of the surfaces, moisture uptake…) that degrade interconnect reliability and performance.

In this talk we will present recent work done on optimization of dielectric etching using CF3I, a promising replacement gas for CF4 in interconnect etch applications. Using a Design of Experiment (DOE) approach through a Taguchi-like Method combined with the capabilities of a State-of-the-Art Unaxis 200mm wafer etch system, the influences of the key parameters on the etching mechanism and performance will be presented. The DOE approach is introduced here to minimize the number of experiments while maximizing the process understanding. For instance, one of the results of the experimental matrix suggests an etching rate contribution of CF3I that is non-linear. In addition to characterization of etch rate, the samples are characterized using RBS, AES and SEM to fully understand the impact of the process parameters on overall film quality. Baseline data as well as structure patterning will be presented after the optimization process using CF3I alone and also using CF3I mixed with well established fluorocarbons.

4:00pm **PS1-TuA7 Challenges in sub-100nm Dual Damascene Etch of Porous Oxycarbosilane Ultra Low-k Dielectrics for BEOL Integration**, ***R.L. Bruce****, S.U. Engelmann, S. Purushothaman,* IBM T.J. Watson Research Center*, T.J. Frot,* IBM Almaden Research Center*, M. Darnon, M. Lofaro, S. Cohen,* IBM T.J. Watson Research Center*, W. Volksen, T.P. Magbitang, L. Krupp, G. Dubois*, IBM Almaden Research Center

There has been much interest recently in porous oxycarbosilane (POCS)-based materials as the interconnect layer dielectric (ILD) in back-end-of-line (BEOL) manufacturing due to their superior mechanical properties compared to conventional porous SiCOH at equivalent porosity and dielectric constant. [1-4] While it is well known that plasma etching and ashing processes can cause significant damage to porous ultra-low k dielectric materials in general, little has been reported about the effect of plasma damage to POCS as the ILD material. In this work, we discuss the effect of plasma etching and ashing processes on POCS during the fabrication of single and dual damascene structures for BEOL integration. We used TEM-EELS to quantify chemical composition changes at the top, bottom, and sidewalls of POCS trenches after each plasma etching and ashing step. After plasma processing, POCS structures undergo extensive plasma damage such as pitting, microtrenching, and the generation of trench bottom roughness. Opening of the cap layer exacerbates these etch damage features. Damage is reduced by increasing the neutral-to-ion ratio of the gas discharge in the ULK trench etch and eliminating O_2 from the ashing process. The use of vapor phase silylation between etch process steps is also shown to repair plasma-damaged POCS. However, we show that the most significant improvement to post-plasma damage occurred by reducing the pore size of the starting POCS material while maintaining comparable porosity, i.e. dielectric constant.

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4:20pm **PS1-TuA8 Mechanism of Highly Selective SiO_2 Etching over Photoresist Using New Alternative Gas, C_5HF_7**, ***Y. Miyawaki****, Y. Kondo, K. Takeda, K. Ishikawa, M. Sekine, H. Kondo,* Nagoya University, Japan*, A. Ito, M. Nakamura,* Zeon Corporation, Japan*, M. Hori*, Nagoya University, Japan

With the continuous demand for increasing the storage capacity of semiconductor memory devices, a much precise etching process for high aspect ratio contact holes in SiO_2 film is indispensable. The aspect ratio of more than 20 will be required for 45-nm node in 2010. Furthermore, deterioration of the SiO_2 selectivity over a fragile, thin photoresist would cause the sidewall roughness and poor pattern-width definition. In this study, we utilized a newly designed environmentally-friendly (low global warming potential) gas, C_5HF_7, and compared the etch performances with conventional C_5F_8 gas. A very-high-frequency (VHF) capacitively coupled plasma (CCP) etcher was used with 1800 W VHF power and 2 MHz bias of 1200 W. C_5F_8 or C_5HF_7 gas was introduced with O_2 and Ar (C_5F_8 or C_5HF_7 /O_2/Ar = 15 / 10-35 / 300 sccm). We evaluated the dependence of O_2 flow rate on the etching rates of SiO_2 and KrF photoresist and SiO_2 selectivity to the resist. The gas phase species, O radical (O*) and CF_3^+, were measured using Vacuum Ultraviolet Laser absorption spectroscopy (VUVLAS) and a quadruple mass spectroscopy (QMS). The C_5F_8 gas chemistry showed the maximum selectivity of 3.7 with the etching rate of 416 nm/min at 20 sccm O_2 flow rate. In contrast, C_5HF_7 chemistry realized much higher selectivity (more than 13.5) with the etching rate of 356 nm/min at 25 sccm O_2 flow rate. It was confirmed that almost four times higher selectivity than that of the conventional C_5F_8 gas was obtained by using the new C_5HF_7 gas. In the both gas chemistry, the density of CF_3^+ ion, that could be one of the dominant etch species for SiO_2, showed the maximum value at the maximum etch rate conditions. The variation trends for O* densities were similar to the resist etch rate in C_5HF_7/O_2/Ar plasma. It was also speculated that the H atoms from C_5HF_7 reduced the density of F radical that would enhance the resist etch rate. The reason for the high selectivity would be examined by measuring the surface chemical compositions and the gas phase species, such as CF_X and F.

4:40pm **PS1-TuA9 Etch Characteristics of SiO_2 in the C_xF_y Dual-Frequency Capacitive Coupled Plasma**, ***M.H. Jeon****, S.K. Kang, J.Y. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

The capacitive coupled plasma (CCP) has been extensively used in the semiconductor industry because it has not only good uniformity, but also low electron temperature. But CCP source has some problems, such as difficulty in varying the ion bombardment energy separately, low plasma density, and high processing pressure, etc. In this reason, dual frequency CCP has been investigated with a separate substrate biasing to control the plasma parameters and to obtain high etch rate with high etch selectivity. Especially, in this study, we studied on the etching of SiO_2 by using the dual-frequency CCP source composed of high (27.12, 60, etc.) MHz/ low (2.0, etc.) MHz rf powers to control the ion flux and ion energy impacting on the substrate independently. By using the combination of high /low rf powers, the differences in the gas dissociation, plasma density, and etch characteristics were investigated.

For SiO_2 etching, fluorocarbon gases are commonly used, because a polymer film which decreases the etch rate is deposited on the silicon surface and enhances the etch selectivity to SiO_2 etching. Therefore, in addition to the frequency variation for SiO_2 etching, the plasma characteristics such as gas dissociation characteristics, plasma density, electron energy distribution, etc. were investigated by varying chemical composition of fluorocarbon gases. With the measurement of plasma characteristics, SiO_2 etching characteristics were also investigated and correlated with the variation of plasma characteristics. The etch rate was decreased with increase in C/F ratio in order of CF_4, C_2F_6, and C_4F_8 plasma, which forms a thicker fluorocarbon polymer on the SiO_2 surface. We observed the increase of CF_2 radicals in the higher C/F ratio plasma by using optical emission spectroscopy (OES). And the etch rates were increased with the low frequency (2 MHz) power for all fluorocarbon plasmas. When the low frequency power was increased, a steady-state fluorocarbon polymer thickness on the SiO_2 surface was reduced by the ion energy during the process, resulting in the increase of the etch rate. The X-ray photoelectron spectroscopic analysis on the surfaces etched by different low frequency powered conditions correlate with the results above.

5:00pm **PS1-TuA10 Ultra-high Selectivity Silicon Nitride Liner Etch: Mitigating Substrate Damage in Logic-based Contact Level Interconnects**, ***A. Metz****, H. Cottle, Y. Chiba, P. Biolsi,* TEL Technology Center America*, M. Luo, E. Geiss,* Global Foundries*, S.H. Sung,* Samsung Electronics*, M. Aminpur, R. Wise*, IBM Microelectronics

5:20pm **PS1-TuA11 Achieving Lithographically Independent sub-35nm Vias for Phase Change Memory Applications**, ***E.A. Joseph****, R. Dasaka, M. Breitwisch, A.G. Schrott, C.H. Lam*, IBM T.J. Watson Research Center

Non-volatile phase change based memory has recently garnered significant interest due to its potential for scalability beyond that of conventional DRAM and Flash memory technologies.[1] However, multiple etch challenges exist in the fabrication of robust PCM devices and not all have been thoroughly discussed and/or researched. For instance, patterning of the novel phase change material without causing material modification and performance degradation is a well known issue and has been reviewed in the past.[2,3,4] On the other hand, the ability to fabricate robust and uniform sublithographic contacts (to the phase change material) is rarely discussed from an etch perspective. In this presentation, this latter issue is explored in detail and a lithographically independent etch process scheme with the capability of yielding sub-35nm vias is presented. Critical factors such as oxide and nitride etch selectivity, taper angle and etch stop phenomenon are all reviewed. Lastly, the application of this method for logic applications such as gate contacts and BEOL via patterning will also be discussed with a focus on the ultimate scaling limitations of this process.

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5:40pm **PS1-TuA12 The Evaluation of Sidewall Polymerization during Platinum Dry Etching Process using Inductively Coupled $Cl_2/O_2/Ar$ and CH_3OH Plasmas**, ***J.Y. Moon***, *J.W. Park, M.S. Lee, B.G. Jyun, W.J. Choi, S.H. Cho, J.S. Roh, S.-K. Park*, HYNIX Semiconductor Inc., Republic of Korea

It has been reported that platinum is the most appropriate resistive switching RAM (ReRAM) electrode material due to its good oxidation-resistance, high electrical conductivity and low leakage current characteristics. However, platinum does not easily form the volatile products, and the unwanted sidewall polymer which is produced during plasma etch process gives a large shift in the pattern size of the etched pattern and also makes it difficult to remove. In this study, experimental studies of platinum etching process have been performed to understand the characteristics of sidewall polymerization using inductively coupled $Cl_2/O_2/Ar$ and CH_3OH plasmas etching process. The effects of etch parameters such as gas combination and substrate temperature on the characteristics of etch properties of platinum were also investigated to minimize sidewall polymer re-deposition in the point of re-deposited sidewall polymers. The thickness of re-deposited polymers related to platinum were measured and studied by high resolution transmission electron microscopy (HR-TEM). The chemical reactions on the etched surface also have been studied by X-ray photoelectron spectroscopy (XPS).

Plasma Science and Technology
Room: Galisteo - Session PS2-TuA

Plasma Sources
Moderator: D.J. Economou, University of Houston

2:00pm **PS2-TuA1 Plasma Study in Modulated Pulse Power (MPP) Magnetron Sputtering with Different Magnetron Configurations**, ***D.N. Ruzic***, *L. Meng, S. Jung, M.J. Neumann*, University of Illinois at Urbana-Champaign

As a derivative of high power pulsed magnetron sputtering (HPPMS), modulated pulse power (MPP) technology is used to apply arbitrary voltage waveforms to the cathode. It not only retains the distinctive features of HPPMS as the intense pulsed plasma density and potentially high ionization fraction of metal atoms, but also offers high degree of freedom for additional process control. In a 1000 cm^2 circular planar magnetron, discharges were initiated using a 10 kW average power MPP generator (capable of a pulse peak power up to 147 kW). To optimize the MPP discharge for the future applications, the effects of pulse waveforms and other discharge parameters on the plasma were studied first using a time-resolved triple Langmuir probe. A typical electron temperature (T_e) of 10 eV and an electron density (n_e) close to 10^{12} cm^{-3} during the pulses were determined. Higher pulse current, lower pulse repetition frequency, higher gas pressure and closer to the target were revealed to exhibit higher n_e, while T_e was also affected. The ion fluxes were then measured using an electrostatic gridded energy analyzer, showing typical ion energies of about 10 eV. Combined with a quartz crystal microbalance, the analyzer was further employed to measure the ionization fractions of sputtered metal atoms under various conditions. Finally, the effects of magnetron configurations were investigated using a specially-designed magnet pack in which both the positions and the strengths of the magnets were fully adjustable. Several configurations showed obvious superiorities to the normal balanced DC magnetron configuration, maintaining a higher pulse current and consequently a higher plasma density. A qualitative plasma model was proposed to explain the observed results and further understand the underlying mechanisms of the MPP discharge.

2:20pm **PS2-TuA2 Spatial Evolution of Plasma Generated VUV in a Microwave Surface-Wave Plasma**, ***J.P. Zhao***, *L. Chen, M. Funk, R. Bravenec, R. Sundararajan,* Tokyo Electron America Inc., *K. Koyama, T. Nozawa,* Tokyo Electron Limited, Japan, *S. Samukawa*, Tohoku University, Japan

Vacuum ultraviolet (VUV) radiations generated in low temperature plasmas (e.g., CCP and ICP) has been reported to cause wafer damage, alteration of morphology of polymers and electrical properties of dielectrics. Electron-hole pairs generated in dielectric films by VUV radiations can be trapped in dielectrics and interfaces. This results in charge buildup and dielectric breakdown as well as the decrease of device reliability. Synergistic effects of VUV exposure and energetic ion bombardment have been addressed to increase photoresist roughening. In order to improve the device and plasma process reliability, monitoring and evaluation of plasma generated VUV radiations have become important and highly demanded in plasma processing. Herein, characterization and spatial evolution of VUV radiations generated in a microwave surface-wave plasma is reported. Microwave surface-wave discharges operating within a wide power and pressure window can be used to produce large area plasmas of high density. Due to its inherent diffusion characteristics, apart from the discharge source, quiescent, uniform, and low-temperature Maxwellian plasma near wafer region can be obtained. In spite of these promising features, understanding the evolution of plasma generated VUV radiations can help the development of microwave surface-wave plasma based hardware and the design of process recipes. The plasma source used in this work consists of a radial line slot antenna (RLSA) which transmits 2.45 GHz microwaves into a large quartz resonator disk which then couples to the plasma. VUV radiations in RLSA plasma are monitored by measuring VUV induced electron-hole pair generation in dielectric films using VUV monitoring sensors developed by Samukawa et al.[1] Three kinds of VUV sensors consisting of SiO_2, Si_3N_4, and SiO_2/Si_3N_4 films are used, which monitor VUV radiations in the wavelength range of <140 nm, <250 nm, and >250 nm, respectively. Measurements in N_2, Ar, and O_2 plasma are carried out from 23 mm to 203 mm below top plate surface. A wide pressure-power spectrum has been investigated. Experimental results indicate that VUV radiations in RLSA plasma are dramatically reduced as a function of distance from the top plate. For better understanding on the evolution of VUV radiations in RLSA plasma, the electron energy distribution functions (EEDFs) are also measured using a Langmuir probe as a function of vertical location. Mechanisms on the evolution of VUV radiations are discussed based on the measured EEDFs and VUV absorption process.

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2:40pm **PS2-TuA3 PM Helicons: A Better Mousetrap**, ***F.F. Chen****, UCLA **INVITED**

Helicon discharges are known to very efficient in generating high plasma densities at low pressures for such applications as etching. The reason for this efficiency is that helicon plasmas depend on resonant waves in a magnetic field which couple the rf energy into electrons in a complicated way involving nonlinear physics. To generate the magnetic field, commercial helicon reactors employ large, heavy electromagnets and a correspondingly large dc power supply to drive them. A new type of helicon discharge has been developed that uses the remote field of annular permanent magnets (PMs) and an array of small tubes that incorporate constructive interference of a reflected helicon wave [1-3]. With 3kW at 13.56 MHz, an 8-tube test device has produced argon plasmas of density 2-6 x 10^{11} cm^{-3} over ~20 x 50 cm areas with +/- 3-5% uniformity [4]. The source needs only 15 cm of vertical space. A code HELIC is used for the design of the wave properties, and a new code EQM has recently been developed to predict the equilibrium profiles of plasma and neutral densities and of electron temperature, With 27.12 MHz it is possible to design a very compact plasma thruster for spacecraft.

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4:00pm **PS2-TuA7 Modeling of a Transformer-type Toroidal Plasma Source**, ***S. Rauf***, *Z. Chen, K. Collins*, Applied Materials Inc.

4:20pm **PS2-TuA8 Self-Consistent Electrodynamics of Large-Area High-Frequency Capacitive Plasma Discharge**, ***Z. Chen***, *S. Rauf, K. Collins*, Applied Materials Inc.

Large-area capacitively coupled plasmas (CCP) generated by high frequency (HF, 3-30 MHz) and very high frequency (VHF, 30-300 MHz) RF sources are used for thin film deposition in the production of thin film transistors for flat panel display and thin film photovoltaic solar panels. Economic considerations are driving a rapid increase in substrate size and adoption of VHF sources for improved film quality and higher deposition rate. As a consequence of these trends, electromagnetic wave effects are

* 2009 Plasma Prize Winner

becoming the dominant factor in determining processing uniformity. Because the effective RF wavelength in plasma depends upon both RF frequency and plasma process conditions such as RF power and gas pressure, a self-consistent model including both RF power delivery system and plasma discharge is highly desired to capture a more complete physical picture of plasma behavior. In this paper, we present a three-dimensional model for self-consistently studying both electrodynamic and plasma dynamic behavior of large-area (> 8 m^2) CCP. The model couples Maxwell's equations with transport equations for charged and neutral species in the time domain. Maxwell's equations are discretized and solved using the finite-difference time-domain (FDTD) method. The plasma discharge is modeled by solving the continuity equations for charged and neutral species and the electron energy conservation equation. The complete RF plasma discharge chamber including RF power delivery sub-system, electrodes and plasma domain is modeled as an integrated system. The RF power source is naturally applied onto the transmission line of the RF feed system in the form of an electromagnetic wave. Based on the full-wave solution model, we are able to study the important limitations for processing uniformity imposed by electromagnetic wave effects in a rectangular reactor having electrode size of 3.05 m × 2.85 m. We examine the behavior of H_2 plasmas in such a reactor at a pressure of 2 Torr when we incrementally scale the frequencies from 13.56 to 200 MHz and the power from 20 kW to 80 kW. We show that various rectangular harmonics of electromagnetic fields can be excited as RF frequency or power is increased. These rectangular harmonics, mathematically described by the hyperbolic functions, can create not only the plasma profiles where plasma density is high at the center and low at the corners of the reactor, but also the profiles where plasma density is high at the corners and along the edges of the reactor and low in the inner area. Such highly nonuniform plasma distribution at VHF or high power level is challenging to compensate and has important implications for large-area plasma processing.

4:40pm **PS2-TuA9 Independent Control of Ion Energy and Flux in CCPs by the Electrical Asymmetry Effect**, ***U. Czarnetzki***, Ruhr-University Bochum, Germany **INVITED**

Technical plasmas are often generated by radio-frequency (RF) fields in the MHz regime. In particular, capacitively coupled RF plasmas have found wide industrial application ranging from semiconductor etching to thin film deposition as e.g. in large area production of solar-cells. In all cases the processes on the substrate surface are critically dependent on the energy and flux of the impinging ions. Therefore, independent control of these parameters is the major aim of various alternative concepts developed in the past. Despite some general progress, in practice independent control has been realized only within certain constrains.

The recently invented electrical asymmetry effect provides a novel solution by adjusting as a control parameter the relative phase between two harmonic RF frequencies [1]. This meets not only the above requirements in an almost ideal way but allows in addition for the first time breaking the symmetry in geometrically geometric discharges, which are common in large area processing. There the phase can be set so that the ion energy is increased on one electrode and reduced on the other or vice versa. The physics of the resulting non-linear system can be reduced to a few basic principles that allow an analytic treatment. The results of the analytical model are compared with particle-in-cell (PIC) / Monte Carlo (MC) simulations and experiments [1-6]. Although the system is characterized by a high degree of complexity all three approaches show remarkable agreements. Ultimately this leads to a detailed understanding not only of the dynamics of the electrical asymmetry effect but also of the physics of capacitively coupled plasmas in general.

Finally, first applications in industry on thin-film solar-cell production demonstrate superior performance by immediately more than doubling the deposition rate of silicon without loss in quantum efficiency.

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5:20pm **PS2-TuA11 Inhomogeneous Magnetic Field Interaction with VHF and HF Capacitively Coupled Plasmas**, ***K. Bera***, *S. Rauf*, *K. Collins*, Applied Materials, Inc.

Both electromagnetic and electrostatic power deposition play important role in very high frequency (VHF) capacitively coupled plasma source to determine the plasma spatial profile. The electromagnetic effect enhances the plasma density near the chamber center, while electrostatic and inductive effects increase the density near the electrode edges. The electrostatic effect prevails for high frequency (HF) plasma sources. Secondary electron emission also plays an important role in determining the HF plasma profile. It has been shown earlier that the plasma profile generated due to VHF and HF sources can be modified using static magnetic fields. In this study, we further investigate the interaction of inhomogeneous static magnetic fields with plasmas. Various magnetic coil configurations, such as solenoid, cusp, mirror and dual solenoids, are considered. Our plasma model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential, $\boldsymbol{A}$, are solved in the frequency domain after every cycle for multiple harmonics of the driving frequency. The electron transport coefficients become tensor quantities in the magnetized plasma. The coupled set of equations governing the scalar potential, Φ, and drift-diffusion equations for all charged species are solved implicitly in time. Static magnetic field from dc current sources has been simulated for different coil configurations, and imported to our plasma model. The plasma modeling result shows that radial magnetic field component limits electron loss to the electrodes and locally enhances the electron density. The axial magnetic field component primarily limits plasma diffusion in the radial direction thereby preserving the effect of improved electron confinement by the radial magnetic field component. For VHF plasmas, using solenoid coil, the magnetic field decreases the electron density in the chamber center and the peak in electron density gradually moves to the edge of the lower electrode. For HF plasmas, the peak density near the electrode edge increases with magnetic field. The effect of magnetic field on the plasma profile is enhanced using the cusp configuration. With dual solenoid, the radial and axial components of magnetic field are modified locally using different coil current ratios and directions. Depending on the nature and location of power deposition in the plasma chamber, the plasma profile is modified in different manner using various coil configurations, current directions, and current ratios.

5:40pm **PS2-TuA12 Properties of Corona Bar Discharges for Production of Preionizing UV Light**, ***Z. Xiong***, *M.J. Kushner*, University of Michigan, Ann Arbor

In electric discharge-pumped excimer lasers as used for photolithography sources in microelectronics fabrication, corona discharges are often used to provide UV photons to preionize the gas mixture. The preionization source, often called a *corona bar*, typically consists of a cylindrical metal rod surrounded by a dielectric. A discharge initiated by a high voltage pulse propagates around the surface of the corona bar, producing a surface-hugging avalanche wave similar to a gas phase streamer. The high electron temperature in the avalanche front produces radiating excited states that in turn produce the desired UV photons. We present results from a numerical study of an idealized corona bar discharge sustained in a multi-atmosphere $Ne/Ar/F_2/Xe$ gas mixture as used in ArF excimer lasers. The corona bar consists of a grounded metal cylinder surrounded by an annular dielectric layer of a few cm diameter. A point electrode (cathode) is located on the surface of the dielectric layer and is subject to a stepwise initial voltage change. The ensuing corona surface discharge was investigated using a 2-dimensional plasma hydrodynamics model with radiation photon transport. Continuity equations for charged and neutral species, and Poisson's equation are solved coincident with the electron energy equation with transport coefficients obtained from solutions of Boltzmann's equation. The ionization front, initiated from the point electrode, propagates along the cylinder surface (with speeds up to 3 x 10^8 cm/s that depend on the dielectric constant) charging the surface as it propagates. The ionization front usually stops before completing a full circle as the corona bar becomes progressively charged. The strength and propagation speed of the ionization wave are characterized by the electron density and temperature distributions along the cylinder circumference. The photon fluxes are collected on a surrounding circular surface. With radiation from short lived states such as Ne_2^*, the UV emission sweeps around the corona bar coincident with the ionization wave. The effects of dielectric constants, gas mixture and voltage on the corona discharge dynamics will be presented.

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Plasma Science and Technology
Room: Southwest Exhibit Hall - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Etching Characteristics of $Ge_2Sb_2Te_5$ in Chemical Effects for the Phase-Change Memory Applications, *J.T. Cheong, H.M. Lee,* ***J.S. Yang****, H.C. Jung, H.C. Lee, Y.S. Sohn, H.S. Kang*, Hynix Semiconductor

The present study aims at providing the fundamental data with respect to GST($Ge_2Sb_2Te_5$) composition and GST damage depending on etch conditions. GST etching in this study was processed by changing etchants. By Cl_2 based GST etching, it was found that, there appeared degradation in the surface roughness due to GST damage, which is identified by XRD(x-ray diffraction) as an unknown phase different from FCC or HCP phases of GST, As for the sample etched by using CF_4 of high ratio and Ar gas, the GST were found damage area where Ge and Sb were deficient in stoichiometry. Meanwhile, GST etch by CF_4 of low ration and Ar gas exhibited the good results of this study, we have demonstrated the damage-free GST etching, which will be applicable for the Phase-Change Memory device.

PS-TuP2 Etch Characteristics of TiN for Metal/High-*k* Gate Stack using Inductively Coupled Plasma, ***J.-S. Park****, J.-C. Woo, C.-I. Kim*, Chung-Ang University, Republic of Korea

The ultra thinned body fully depleted silicon on insulator (UTB-FD SOI) is the solution to problems of short channel effect by shrinking the gate length. This device has many advantages of high drive current, high conductance and ideal sub threshold slope[12]. This device uses the TiN/HfO_2 gate stack . The metal/high-*k* stack structure is being the core technology because reduction of device is faced with physical limitations.

So, we have to study about this metal/high-k stack[3].

In this study is investigated the dry etching characteristics of the TiN in the TiN/HfO_2 gate stack using inductively coupled plasma system. TiN thin film is etched by CF_4/Cl_2/He plasma. We investigate the etching chemistry of the CF_4/Cl_2 gas mixture. Etching parameters are gas mixing ratio, the RF power, the process pressure in this study. The chemical reactions on surface of the etched TiN and etched HfO_2 are investigated by X-ray photoelectron spectroscopy. The profile of the etched TiN is investigated by Scanning electron microscope.

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PS-TuP3 Etch Characteristics of $HfAlO_3$ Thin Films in High Density Plasma, ***T.-K. Ha****, J.-C. Woo, C.-I. Kim*, Chung-Ang University, Republic of Korea

With the permanent scaling down of complementary metal oxide semiconductor (CMOS) devices, the thickness of the gate oxide is expected to be reduced to less than 1 nm for the 45 nm and 32 nm technology nodes. Continuing to reduce the gate insulator thickness using SiO_2 is problematic as gate leakage current due to direct-tunneling increase.[1-2] One solution to the problem is the replacement of SiO_2 by high-*k* material. $HfAlO_3$ have arisen as a promising material for gate oxide replacement due to their high dielectric constant, bandgap, and recrystallization temperature. Therefore, a further on the study of $HfAlO_3$ thin films is needed.[3]

In this work, $HfAlO_3$ thin films were etched in BCl_3/He plasma. The etching characteristics of $HfAlO_3$ thin films were investigated in terms of etch rates and selectivity as a function of gas mixing ratio, RF power, DC bias voltage, and chamber pressure. The total flow rate of BCl_3/He was fixed at 20 sccm. The other parameters were varied as follows; RF power = 400 ~ 600 W, DC-bias voltage = - 50 ~ - 200 V, process pressure = 1 Pa ~ 3 Pa. The plasma diagnosis was characterized by optical emission spectroscopy (OES) analysis. The chemical reaction on the surface of the etched the $HfAlO_3$ thin films was investigated with X-ray photoelectron spectroscopy (XPS). Field emission scanning electron microscopy (FE-SEM) was used to investigate the etching profile.

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PS-TuP4 The Dry Etching of ITO Thin Films on Glass for Flat Panel Displays, ***J.H. Wi****, J.-C. Woo, C.-I. Kim*, Chung-Ang University, Republic of Korea

Amongst the most widely employed thin films in Flat Panel Displays (FPDs) belong to the described as Transparent Conducting Oxide (TCO) materials. When the thin films were applied for devices, etching characteristics is important process factor due to availability of patterning is directly linked with productivity. The TCO materials should have to proper etching characteristics for transparent electrode[1]. By far the most common industrially employed TCO is Indium Tin Oxide (ITO), which is more correctly described as Sn-doped In_2O_3. An n-type semiconductor, it offers an optimum performance in terms of conductivity and transparency. In order to utilize properties of thin films such as ITO it is usually necessary to pattern them to create functional structures. The conventional method for patterning is to use wet chemical etch process. Such techniques require multiple process stages, large expensive machinery, small-geometry patterning[2].

In this study, the relationship between patterning characteristics and other characteristics which depend on etch conditions, especially the RF power, the DC bias voltage, the process pressure, was investigated in ITO films etched by the inductively coupled plasma (ICP) system[3]. The analysis of x-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical reactions between the surfaces of ITO thin films and etch species.

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PS-TuP5 Effect of N_2/Ar Flow Rates on Surface Roughness during High Speed Thinning of Si Wafer using F Radicals and NO Gas, ***W. Heo****, N.-E. Lee*, Sungkyunkwan University, Republic of Korea

In this work, we investigated on evolution of the surface roughness and morphology of thinned Si surface and die strength of thinned Si during high-speed chemical dry thinning of Si wafers ground by chemical mechanical polishing down to 100 mm. The direct injection of NO gas into the reactor during the supply of F radicals from NF_3 remote plasmas was very effective in increasing the Si thinning rate above 22.8 mm/min, due to theNO-induced enhancement of the surface reaction,but resulted in the significant roughening of the thinned Si surface. However, the addition of directly-injected N_2/Ar gas, together with NO gas, decreased the root mean square (RMS) surface roughness of the thinned Si wafer significantly. Therefore, rough surfaces of mechanically ground Si wafers could be effectively smoothened by adjusting the additive gas flow rates of N_2/Ar during chemical dry thinning of the Si thickness larger than 50 mm. We also measured mechanical strength of thinned Si wafer in order to understand the effect of chemical dry thinning on removal of mechanical damage generated during mechanical grinding. Fracture strength of the thinned Si wafers was measured using 3-point bending test and compared. The results indicated that chemical dry thinning with reduced surface roughness and mechanical damage effectively increased the fracture strength of the thinned Si wafer. It is expected that high-speed dry chemical thinning process has possibility of application to ultra-thin Si wafer thinning with controlled surface roughness and mechanical damage removal after mechanical grinding of silicon wafer.

PS-TuP6 Modelling of the Silica Glass Etching under ICP SF_6/Ar Plasma Discharge, *L. Lallement,* ***A. Rhallabi****, M.C. Fernandez, C. Cardinaud*, Institut des Materiaux Jean Rouxel, France

Quartz or pure fused silica is selected material for the fabrication of biochip devices and more specifically electrophoresis chips. Indeed, these materials benefit from transparency in the UV-visible range, and low dielectric breakdown. However material cost is higher in comparison to silica glass which offers similar properties with a low purity degree. Plasma deep etching techniques are well established for fused silica and quartz, but much more challenging for glass. In the present study, the etching simulator has been developed to study the etching of silica glass (Pyrex, D263, AF45, and Vycor) in SF_6/Ar plasma. The etching model is based on the development of the plasma kinetic model coupled to 2D Monte Carlo surface model to predict the etched surface morphology of glasses as a function of the operating conditions.

The gas phase kinetic model is based on the mass balance equations of reactive species. The kinetic constants of electron impact reactions are established as a function of electron temperature assuming maxwellian distribution of electron energy. The additional equation of power balance in the ICP reactor allows to determine the electron temperature evolution with the plasma discharge parameters (Rf power, reactor pressure and SF6/Ar flow rates).

Langmuir probe is used to measure the electrical parameters of SF6/Ar plasma mixture such as, electron temperature and density as a function of the plasma discharge parameters. A good agreement between the simulations and the experiments have been observed

One of the advantages of our model is the coupling between the plasma chemistry model and the surface etching model. The later is based on the Monte-Carlo approach which allows to describe, in a probabilistic manner, the surface mechanisms for silica glass etching.

The direct fluxes of the reactive species such as fluorine and ions are determined from the gas phase kinetic model and introduced as the input parameters in the glass etching model.

On the other hand, surface analyses such as the etch rate, surface roughness (profilometry), and surface topography (AFM) of silica glass as a function of operating conditions have been carried out.

The preferential redeposition mechanism of the etched products on the metallic sites seems to play an important role on the propagation of the etched surface roughness. A satisfactory agreement between experimental results and the model concerning the etching rate and the etched surface morphology have been obtained for different glasses.

PS-TuP7 Impact of Neutral Particles Ballistic Delivery Upon Sidewall Profile Formation During Dry Etching, ***S.I. Yanovich****, V.A. Khrustalev, O.P. Gushchin, A.M. Islyaykin, E.V. Danilkin, S.I. Patyukov, A. Smirnov*, Mikron JSC, Russia

Dry etching is a key process for topology formation and integrated circuit layers layout transfer on to a semiconductor substrate. Forced by Moore 's law challenging demands dry etching technique was improved drastically for the decades. Development of fundamental plasma processing knowledge provides technical staff with the ideas for their engineering efforts in getting the right hardware supported by right process recipe. Nevertheless there is still a room for further dry etching process development to fit the requirements of a variety of particular silicon, compound semiconductors, MEMS, fluidics and other application.

This paper presents an extension of a general model for plasma dry etching process in respect of impact of neutral particles delivery to the substrate surface and its influence on final window profile depending on window linear dimension. It is found that different size windows may have different side wall slope and bottom profile within the range of windows that might be present at actual IC layout of quarter micron mode and beyond. In many cases such a difference of etched profiles it is considered that neutral particles lateral delivery sheltering is responsible.

This effect is intrinsic for different dry etching processes including silicon dioxide etch, silicon etching, aluminum and its alloys etch. Sloping sidewall profile for larger lateral dimension of etched window may be considered both as advantage and disadvantage depending on each particular case. And therefore it is important to review precisely each case of window size extension or isolated element location and the elements located at array edge as well.

PS-TuP8 Using Pulsed Bias to Explore 2 µm AR 25:1 TSV, ***M. Kostermans***, IMEC, Belgium, *M. Brouri*, Lam Research Corporation, Belgium

Since traditional 2-D planar architecture of ICs inevitably imposes restrictions on miniaturization, new interconnection and packaging technologies need to be developed to keep on track with the continuously scaling of electronic systems. 3-D integration is an interesting solution since it allows for reduction of the system size, both in area and volume. Furthermore, it improves performance since 3-D interconnects are shorter than traditional interconnects in a 2-D configuration, enabling a higher operation speed and smaller power consumption.

Plasma processing for dry etch purposes traditionally rely on a few basic parameters, allowing control of the discharge physics and chemistry: plasma power, substrate bias, flow of different gases, total gas flow, discharge pressure. In order to ensure a reliable pattern transfer, a basic requirement for the etch mechanism is to provide anisotropy. This means that patterned features usually need to be etched with vertical sidewalls, i.e. as little undercut/bowing/slope as possible. This can only be achieved, on one hand, by carefully tuning the plasma chemistry, in order to provide passivating species that will deposit on the feature sidewalls and protect them, and on the other hand by controlling the ion energy, which contributes to the removal of this passivating film on horizontal surfaces.

Another possibility to influence plasma characteristics is by pulsing the substrate bias power at different frequencies and duty cycles. Although deep Si via processes have been developed using this technology, little is known on the influence of the pulsing on etch rates, film selectivities, polymerisation curves, ... for state-of-the-art processes. For this study bias pulsing frequencies with different duty cycles are employed, in addition to the traditional deposition and etch Bosch cycles. The first step is C_4F_8 based and acts as a deposition step which passivates the via bottom and sidewall and enhances the resist selectivity. The second step, using SF_6, is the actual etch step.

This study investigates the use of pulsed bias applied to the development of 2 µm diameter vias with an aspect ratio up to 25:1 taking into account profile, resist selectivity, roughness, bowing ... When varying the pulsing settings an impact on profile slope and resist selectivity is observed.

The resist based etch development was done on a ICP etch chamber optimised for deep Si etch (Lam Research 2300®Syndion®). The process used in the ICP etch chamber consists of two fast switching steps that are continuously repeated. To enable subsequent metallisation, these vias need to meet strict requirements.

PS-TuP9 Highly Selective and Low Damage Etching of TiN on HfO_2 Layer Gate Stack Structure using HBr/Cl_2 Neutral Beam, ***J.K. Yeon****, W.S. Lim, Y.Y. Kim, B.J. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

As the critical dimension of metal-oxide-semiconductor field-effect transistor (MOSFET) shrinks to 45 nm and below, conventional poly silicon gates on ultrathin SiO_2 dielectric layers need be replaced by metal gates on high-k dielectric materials. However, the successful adoption of these new materials imposes new integration problems. Among many integration issues, selective etching of metal gate electrodes and the high-k gate dielectrics over the Si substrate is expected to be one of the critical steps in the process integration of the front end of the line. In the case of TiN etching on HfO_2 layer using conventional RIE etching, HfO_2 layer can be electrically damaged by charged particle leading to higher leakage current, the change of threshold voltage, etc. In order to solve these problems, in this study, we investigated etch characteristics of TiN on HfO_2 layer using low angle forward reflected neutral beam and compared with those by conventional RIE etch process.

As a result, we observed nearly unlimited etch selectivity of TiN/HfO_2 uisng HBr/Cl_2 gas mixing neutral beam by controlling energy (<100 eV). Also, using TEM and AFM, we observed an anistropic etch profile and smooth surface roughness (0.109 nm). Neutral beam for metal gate etching process turns out to be very promising for gate/high-k dielectric complementary MOSFETs due to lower interface trap generation during etching process.

PS-TuP10 Atomic Scale Etch Depth Control and Low Damage Etching of III-V Compound Materials using Cl_2 Atomic-Layer Etching, ***Y.Y. Kim****, W.S. Lim, J.K. Yeon, T.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

PS-TuP11 Surface Model for Profile Simulation of SiO_2 Etching in Fluorocarbon Gas Chemistry, ***T.Y. Yagisawa****, T.M. Makabe*, Keio University, Japan

As the size of ULSI elements shirinks further, functional design for a top-down plasma processing will be strongly needed in order to solve many types of technological difficulties induced by plasma etching. Actually, under the present design rule for DRAM devices, a contact hole with high aspect ratio (> 20) is required.

The reactive ion etching (RIE) of high aspect contact hole (HARC) or inter layer dielectric has been traditionally performed by fluorocarbon gas chemistry in a two-frequency capacitively coupled plasma (2f-CCP) reactor. As is well known, SiO_2 etching in fluorocarbon chemistry proceeds under the competition of surface protection by the deposition of C_xF_y radicals and chemical sputtering by directional CF_x^+ ions. Under a practical condition for SiO_2 etching where the radical flux is larger than that of ions, a reactive mixing layer (SiO_xF_y), formed under excessive F radicals assisted by high-energy ion bombardment, is always covered with thick polymer layer (C_xF_y). Consequently, the etching is essentially carried out through the removal of polymer layer and the chemical reaction in a mixing layer. The side wall is simultaneously protected against the energetic ions by C_xF_y polymer deposition.

Under the circumstance, we have developed the two-layer sufrace model for the simulation of SiO_2 etching profile in fluorocarbon gas chemistry. This model clarified the effects of reactive species (ions and radicals) on the SiO_2 etching profile [1] and the dependence of etch rate on the pattern size (RIE-lag) [2].

In this paper, we will propose a new surface model for SiO_2 etching which accounts for the selectivity between SiO_2 and underlying Si substrate in HARC processing. Feature profile evolution and the selectivity during SiO_2 etching can be coincidentally discussed as functions of flux of reactive species and impact ion energy. In addition, the effect of resist mask erosion will also be discussed.

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PS-TuP12 General Approach to Feature Profile Evolution via Monte Carlo Simulations, *P.E. Moroz,* TEL US Holdings, ***P. Miller***, HFS

This report will discuss numerical techniques used in the general feature profile evolution simulator FPS-3D. We call it general because it does not have any hardcoded dependencies, such for example, as etch or deposition rates, or dependencies on energy or angle of incident reactive particles (ions as well as neutral radicals and gases). The code thus can be applied to targets consisted of any set of solid materials and exposed to any fluxes of reactive particles with any distribution on energy and angle. Although the code is called FPS-3D, it actually has two options, 2D and 3D, which allow convenient comparison between 2D and 3D results for similar targets and fluxes. The 2D option has advantage of much higher speed of calculations, mainly because the number of cells is typically much smaller and the calculations are simpler than that for 3D, but the 3D option becomes indispensable when the target cannot be approximated by 2D geometry, or when the essentially 3D tasks are considered, such as roughness, for example. The FPS-3D code can comfortably treat up to one million cells, or maybe, a few times of that, depending on the speed of a computer. Correspondingly, the 2D option of FPS-3D allows consideration of a wide range of target sizes, from nanometers to micrometers, as well as treating them in great detail, such for example, as 1000x1000 cells. For the 3D option, a typical run is limited to about 100x100x100 cells, thus leading to each cell containing significantly more molecules than for 2D. One of the main advantages of FPS-3D relative to all other similar software is its GUI-graphics interface based on the TPSOFT package from HFS [1]. This interface is capable of producing high-speed and high-quality 2D and 3D graphics not only for initial parameters, distributions, geometry and fluxes, but also dynamically while the code is running and the feature profile and other parameters evolve, with a unique characteristic of not slowing down the calculations. The authors are thankful to S.-Y. Kang of TEL TDC for valuable discussions.

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PS-TuP13 Warm Magnetized Vlasov Emission Equilibria, ***R.E. Terry***, Naval Research Laboratory (retired)

A Vlasov equilibrium is developed for steady state emission into a magnetized gap in coaxial geometry. The cathode boundary conditions are those of a perfect conductor that emits a Maxwellian electron flux radially, azimuthally, and axially. The anode boundary conditions are those of a perfectly absorbing conductor. The cathode carries a fixed current and the radial gap is set to a fixed voltage. The angular momentum of emitted electrons around the cathode is found to materially change the orbit turning points. When energy conserving solutions are examined it is found that axial velocities must remain bounded above by a well defined function of radius, magnetic field, and voltage. A fully nonlinear and self consistent Vlasov-Poisson problem is formulated and solved for the space charge distribution implied by the Vlasov equilibrium. Moments of the Vlasov distribution then determine the shunt impedance of the gap and the criteria for "warm" magnetic insulation of the coaxial line. The theory limits to Ottinger's critical current magnetization picture for cold electrons, but shows a properly non-singular behavior in the electron density profile at the radial turning points and so properly reduces the enhancement of ion flux across the gap. Extensions of the model to include electron impact ionization of neutrals in the gap are also developed.

PS-TuP14 Inductive Plasmas in Cl_2/Ar : Comparison of Hybrid Model Results with Experimental Measurements, ***J.-P. Booth***, *E. Despiau-Pujo, R. Sarot, P. Chabert,* CNRS-LPP, France*, L. Gatilova, S. Bouchoule*, CNRS-LPN, France

Inductively-coupled chlorine-based plasmas (often also containing HBr, O_2 and Ar) are widely used in the microelectronics industry for selective, anisotropic etching of silicon, and are currently being investigated for etching of III-V materials such as InP for the fabrication of photonic devices.

We have constructed a reactor, identical in geometry to an industrial 200mm etch tool, but adapted for advanced diagnostics and supplied with Cl_2/HBr/O_2 and Ar gases. It is excited by a flat spiral antenna though a dielectric window. In parallel we are developing a hybrid simulation code based on the HPEM (Hybrid Equipment Plasma Model) of Mark Kushner. Experimental measurements of internal plasma parameters (electron densities, temperatures, and also gas dissociation fraction and temperature) will be used to test and improve the simulation code. The aim is to reliably predict the plasma behaviour as a function of these parameters, and for arbitrary reactor geometries.

The electron density was measured using a microwave hairpin resonator, and with a Langmuir probe. Measurements were made as a function of pressure and power in pure Cl_2 and as a function of composition in Cl_2/Ar mixtures. The electron density decreased from $5x10^{10}cm^{-3}$ to $2x10^{10}cm^{-3}$ as the Cl_2 pressure was increased from 0.5 to 10 mTorr. The electron density also decreases monotonically as the Cl_2 fraction is increased in Ar/Cl_2 mixtures. The Langmuir probe measurements of n_e showed the same trend as the hairpin probe, but gave lower values, particularly at the highest pressures and lowest powers and for high Cl_2 fractions.

PS-TuP15 Computer Simulation of a Controllable Electron Beam Exciter, ***D. Urrabazo,*** *M.J. Goeckner, S. Thamban,* University of Texas at Dallas*, G. Padron-Wells*, University of Texas ar Dallas

We have developed a new chemical diagnostic based on a controlled electron beam. Specifically we make use of an inductively coupled plasma, electron extraction optics and traditional optical emission spectroscopy. In the work reported here, we make use of a computer simulation using the Comsol to investigate system characteristic and enhance the system performance. The axially-symmetric spatial distributions of the particle densities and electron temperature are calculated for varying pressure and power regimes. These simulation results will be compared to electrical probe measurements gathered from the experimental apparatus. This work is supported in part by NSF (Grant CBET- 0922962) and Verity Instruments.

PS-TuP16 Numerical Simulations of a Magnetron Plasma Sputtering System using VORPAL, ***C.M. Roark***, *C. Zhou, P.H. Stoltz*, Tech-X Corporation

Three-dimensional numerical simulations are conducted for a magnetron sputtering plasma and target using the particle-in-cell code VORPAL. These simulations require accurate models of particle dynamics, Monte Carlo collisions and self-consistent electric and magnetic fields. The sputtering yield is calculated for materials commonly used in industrial applications. Sputter patterns are compared with experimental measurements, and in particular, we discuss non-uniformities in the sputter patterns and compare with the cross-corner effect. We also discuss the role of charge exchange and elastic scattering on the sputter patterns.

PS-TuP17 Multivariable PID Control of Oxygen and Fluorine Radicals in an Argon/Oxygen/Fluorocarbon Plasma, *B. Keville,* ***M. Turner***, *A. Holohan*, Dublin City University, Ireland

Plasma enhanced processes such as etching are generally run open loop and hence are sensitive to disturbances such as substrate loading, wall effects and matching network drift. The deleterious effect of disturbances on process reproducibility could be mitigated by effective closed loop control of important reactive species in the plasma. The design of effective control algorithms is facilitated by control-oriented models of the causal relationships between plasma species to be controlled and actuators such as flow rate setpoints. For example, it may be demonstrated both experimentally and through simulation that the relationship between oxygen flow rate set point at the mass flow controller and atomic oxygen density in an oxygen plasma may be modelled adequately by a linear second order plus time delay (SOPTD) transfer function. Single input, single output (SISO) SOPTD processes may be controlled very effectively with a Proportional-Integral-Derivative (PID) controller. Suitable parameters for the controller may be determined using well established frequency domain methods such as Pole-placement, root –locus and frequency response, amongst others. Closed loop robustness to unmodelled dynamics, measurement noise and exogenous disturbances may be quantified by stability margins. Simultaneous control of two or more reactive species in a multigas plasma is a vastly more difficult problem due to the inherent multivariable nature of the problem. There are phenomena that arise in multi-input-multi-output (MIMO) systems that do not occur in SISO processes. In particular, due to interaction between variables, instability may arise in a multiloop PID control structure despite each loop being individually stable. Classical, frequency-based SISO design methods do not transfer directly to MIMO systems, and although a number of attempts have been made to adapt classical methods to MIMO systems, MIMO PID control remains relatively immature in comparison to the single variable case. MIMO PID represents a very fertile and active research area and this presentation considers application of current research to the simultaneous control of oxygen and fluorine radicals in an argon/oxygen/fluorocarbon plasma.

PS-TuP18 An Experimental Demonstration of Real-time Closed-loop Control of a Capacitively Coupled Argon Oxygen Plasma, ***Y. Zhang**, B. Keville, A. Holohan, M. Turner, S. Daniels*, Dublin City University, Ireland

Plasma processing of materials for advanced manufacturing is a key enabler for synthesis of nanoelectronic systems. In mainstream IC manufacturing, plasma processing is routinely used in etch and deposition steps. However, ensuring process repeatability and reproducibility is a major challenge for the IC manufacturing industry. Processing tools are, in general, run in open loop control mode and plasma parameters such as ion flux and radical densities at the substrate surface are sensitive to drift in tool subsystems, changes in wall condition and wafer loading, for example. Disturbances to key plasma parameters may affect process metrics such as etch depth and anisotropy and result in a significant degradation in device yield and performance. Hence, process reproducibility may be improved significantly by effective closed loop control of the plasma process.

In this work we present an experimental demonstration of closed loop control of a capacitively coupled Ar/O2 plasma using an optical emission spectrometer and a hairpin resonance probe as sensors. Design of the control algorithm is facilitated by a process model, which has been derived from a physics-based model and validated by taking step responses experimentally. The efficacy of the algorithm is demonstrated by setpoint tracking and disturbance rejection over a range of operating points.

PS-TuP19 Real Time Closed Loop Control of Plasma Processing, ***B. Keville**, M. Turner, S. Daniels, Y. Zhang, A. Holohan*, Dublin City University, Ireland

In general, real time, closed loop control of plasma assisted processes has not been applied in IC manufacturing. In the case of etching, 'process control' is generally understood to mean ex situ statistical analysis of metrics such as etch depth, uniformity, anisotropy and selectivity and consequent adjustment of the process recipe, which is specified in terms of inputs such as gas flow rates, forward power and pressure. An alternative approach would be to specify a recipe in terms of plasma parameters such as ion fluxes and radical densities at the wafer surface and to regulate these in real time by adjusting the inputs with a suitable control algorithm. Such an approach would mitigate potential plasma process disturbances such as wall seasoning and substrate loading, leading to an improvement in process reproducibility. This presentation describes how suitable control algorithms for low pressure plasma processes may be derived from control-oriented process models. The stability and efficacy of the control algorithms are demonstrated using an plasma simulation. Some parameters of the control algorithm depend on unknown, possibly time-varying process parameters such as wall sticking coefficients. The presentation indicates how, given a process model and process measurements, the control algorithm may be adapted/gain-scheduled in order to maintain stability. Experimental implementation of control algorithms on a capacitively coupled plasma is presented and the results are compared to those of the simulation.

PS-TuP20 Adhesion Improvement of DLC Films on Polymer Substrates, ***S.-M. Baek**, T. Shirafuji, S.-P. Cho, N. Saito, O. Takai*, Nagoya University, Japan

Recently, diamond-like carbon (DLC) films have been performed on polymer substrates for improving scratch resistance and gas barrier properties. However, the DLC films deposited directly on polymers often encountered the problem of poor adhesion, which can reduce the performance of the DLC films. Low adhesion of the DLC films is recognized as a consequence of a residual stress due to high atomic density in comparison to polymers. Plasma pre-treatment is one of the most effective methods to modify the top surface of polymers involving surface cleaning, ablation and surface chemical functionalization. Since the bonding states of the interface are formed at the initial stage of the film growth, the adhesion strength of the films is controlled by the condition of plasma pre-treated surface. However, there have been few reports that directly dealt with the relation between the interface properties and adhesion of the DLC films.

In this study, the DLC films have been prepared on polyethylene terephthalate (PET), polycarbonate (PC) and (PMMA) substrates using a pulse biased ICP-CVD method. Plasma pre-treatments using Ar, O_2, CO_2, N_2 and CH_4 gases were performed on polymer substrates prior to DLC (non-doped, Si-doped, and oxygen-doped) coatings. The plasma pre-treated surfaces have been investigated by XPS and FT-IR ATR. The adhesion of the DLC films on polymer substrates has been characterized with a scratch test method. The scratched areas have been observed with optical microscope and SEM. Regarding the adhesion on the PET, at this moment, the doping oxygen in the films and the plasma pre-treatment have shown no effects on the adhesion of the DLC films. On the PC, on the other hand, the oxygen incorporation in the Si-doped DLC films has resulted in the enhanced adhesion of films. Furthermore, formation of the interfacial layer with N_2-plasma pre-treatment has markedly increased the adhesive strength of the DLC films on the PMMA.

Since the nitrogen atoms or NH bonds are considered to be a key factor to improve the interfacial adhesion properties, we have examined formation of the Self-Assembled Monolayer (SAM) which has NH groups at the top of the SAM. The SAM is composed of a bundle of relatively long molecular chains. Thus, we can expect the SAM layer to have mechanical flexibility. This will brings about further improvement of the adhesion properties of the DLC films, such as prevention of film-peeling due to thermal history, which is now under investigation.

PS-TuP22 2m Long-Linear Plasma Production by Microwave in a Narrowed Rectangular Waveguide with a Long Slot Antenna, ***H. Shindo**, Y. Kimura*, Tokai University, Japan

Long line-shaped plasmas are inevitable in material processing in manufacturing industries, such as solar cell film CVD, flat panel displays (FPDs), and various surface modification of large-area thin films. In this work, a newly proposed method of large-scaled line plasma production is studied. In this method, microwave power of frequency of 2.45 GHz in a narrowed and flattened rectangular waveguide is employed to produce a long uniform line plasma. Since the width of waveguide is very close to the cutoff condition, the wavelength of microwave inside the guide is very much lengthened, providing a condition of long line high density plasma with a great uniformity.

The narrowed rectangular wave-guide of 1.0 and 2.0 m in length and 5mm in height were prepared and the width of the waveguide is 62.0 to 61.5 mm which is very closed to the cut-off condition. The waveguide has a long slot on the top surface to launch the micro-wave into the discharge plasma chamber of 1.0 and 2.0 m in length. At the end of wave guide, a short plunger was quipped to adjust the phase of the standing microwave, hence the uniformity of the plasma thus produced. The plasmas of Ar at the pressures of 100 to 500 mTorr were produced by employing an extremely long microwave wavelength. The plasma thus produced was three-dimensionally measured by a Langmuir probe.

The axial profile of electron density in the plasma thus produced was quite flat and as the microwave power is increased, the uniformity becomes improved. In particular, the uniformity within 4 % was attained in the entire plasma of 2 m in length in the condition of microwave power above 1000 W. This kind of uniform linear plasma production showed a threshold in the microwave power, above which the electron density becomes high enough above the cut-off density of microwave of 2.45 GHz. It was also found that the profile of electron density was adjustable by the short plunger. To be specific, the electron density measured at a fixed Z position showed a standing wave-like profile, indicating the short plunger has functions of standing wave generation as well as the phase-shifter as expected. Thus we conclude that the present method of large-scaled linear plasma production is quite advantageous for large area processing.

PS-TuP23 A Study on the Characteristics of Multi-Hole Electrode RF Capacitive Discharge and its Application to Large Area Process, ***H.S. Lee**, Y.S. Lee, H.Y. Chang*, KAIST, Republic of Korea

Multiple-hole electrode RF capacitively coupled plasma source is experimentally characterized and the large area application of the plasma source is experimentally shown. The plasma density enhancement was measured at various pressure, hole diameter, RF current and gas species condition. The bulk plasma intrusion in the hole and the ionization avalanche in the sheath region facilitated high density plasma generation for fixed power when the diameter of the hole was slightly bigger than triple the sheath length. From the analysis of the multiple hole electrode RF capacitively coupeld plasma, the condition to make uniform plasma density over large area plasma source is sought and analyzed. By use of the technique, high density and uniform large area capacitively coupled plasma discharge become possible.

Plasma Science and Technology
Room: Galisteo - Session PS+MN-WeM

Plasma Processing for 3D Integration, TSV, and MEMS
Moderator: M. Darnon, CNRS-LTM, France

8:00am **PS+MN-WeM1 High Etch Rate of TSV using by Ultra Self-Confined VHF-CCP**, ***Y. Morikawa***, *M. Yoshii, N. Mizutani, K. Suu*, ULVAC, Inc., Japan

Thru silicon via (TSV) etch process for deep and high-aspect ratio structure has been studied thoroughly for applications such as MEMS devices. Recently, TSV used in 3D-LSI devices, the via diameter and depth would be several tens of microns, and, the package for CMOS image sensors using TSV may have via diameters and depths up to 100 microns. A diameter of above 50um account for 50 % of TSVs. Therefore, development of high etch rate about 50um via is very important for realizing these applications. In this study, a large via size of 50 um etching in a low-pressure process was focused by using very high frequency capacitive coupled plasma (VHF –CCP) with an ultra self-confined system. This plasma system is simple parallel plate CCP. And the cathode has a structure designed to minimize the stray capacitance (Cs) and impedance (L) to get a low-pressure process of about 100Pa or more. Low-pressure process was carried out on the plasma confined, because mean free pass is very short. And, ion energy distribution (IED) is also controllable by low-presser process with VHF bias. The bimodal IED changes under low-pressure. The peak of high-energy side is reduced, and a charge exchange peak appears. It is considered that the charge exchange is important to anisotropic Si etching with VHF bias. Finally, an etch rate of more than 60 µm/min was realized. It was found that the Si etch rate depended on fluorine radical density and ion energy distribution, so, the high rate was obtained by creating a high fluorine radical density condition by using a high pressure condition of 100Pa using a VHF-CCP reactor with an ultra confined system and SF6 gas chemistry.

8:20am **PS+MN-WeM2 Very Uniform and High Rate TSV Etching Process in Advanced NLD Plasma**, *Y. Morikawa*, ***T. Murayama***, *K. Suu*, ULVAC, Inc., Japan

The h igh-density of thru silicon via (TSV) is indispensable to the utilization and improvement in performance of 3D-LSI. Advanced high aspect ratio TSV etching technologies are required for high-density TSV formation. We have developed a new etching system for TSV application. This s ystem is a planer type magnetic neutral loop discharge (NLD) plasma, which is named as advanced NLD. For high rate silicone etching, it is very important to understand not only the high density of the plasma generation but also the high density of fluorine atoms . In this study, a novel RF antenna ‘ M ulti Stacked rf A ntenna’ has also been developed for the purpose of high rate etching. This antenna consists of multistage spiral turn rf antennas to reduce self- inductance (L), and is increased from turn of spiral to extend the inductive coupling discharge region. T he L feature of this antenna is 0. 95 uH and it is a low L antenna compared to the standard spiral antenna (1.7uH) . As a result of performing the electron density measurement of the NLD plasma using this MS antenna, it succeeded in the high-density plasma production of $1x10^{12}$ / cm^3 by the process pressure of 7 Pa. Next, the Si etching process development was performed using the a dvanced NLD etcher. Si etching characteristics employing advanced NLD plasma were studied with respect to distance from an antenna. As a result, the etching rate improved 4 times more compared to the standard NLD. Finally, the diameter of 1 .5 um was attained by the anisotropic etching of 8. 5 um/min, and the aspect ratio is 5.3 using the a dvanced NLD etcher.

8:40am **PS+MN-WeM3 Deep Reactive Ion Etch Process Optimization for Control of Sidewall Profile and Morphology as a Function of Aspect Ratio**, ***R.J. Shul***, *R.L. Jarecki, T.M. Bauer*, Sandia National Laboratories, *M. Wiwi*, LMATA Government Services

9:00am **PS+MN-WeM4 XeF_2 Vapor Phase Silicon Etch used in the Fabrication of Movable SOI Structures**, ***J. Stevens***, *R.J. Shul*, Sandia National Laboratories, *M. Wiwi, C.L. Ford*, LMATA Government Services, *T. Plut, T.M. Bauer*, Sandia National Laboratories

Vapor phase XeF_2 has been used in the fabrication of various types of devices including MEMS, resonators, RF switches, and micro-fluidics, and for wafer level packaging. In this presentation we demonstrate the use of XeF_2 Si etch in conjunction with deep reactive ion etch (DRIE) to release single crystal Si structures on Silicon On Insulator (SOI) wafers. XeF_2 vapor phase etching is conducive to the release of movable SOI structures due to the isotropy of the etch, the high etch selectivity to silicon dioxide (SiO_2) and fluorocarbon (FC) polymer etch masks, and the ability to undercut large structures at high rates. Also, since XeF_2 etching is a vapor phase process, stiction problems often associated with wet chemical release processes are avoided. Monolithic single crystal Si features were fabricated by etching continuous trenches in the device layer of an SOI wafer using a DRIE process optimized to stop on the buried SiO_2. The buried SiO_2 was then etched to handle Si using an anisotropic plasma etch process. The sidewalls of the device Si features were then protected with a conformal passivation layer of either FC polymer or SiO_2. FC polymer was deposited from C_4F_8 gas precursor in an inductively coupled plasma reactor, and SiO_2 was deposited by plasma enhanced chemical vapor deposition (PECVD). A relatively high ion energy, directional reactive ion etch (RIE) plasma was used to remove the passivation film on surfaces normal to the direction of the ions while leaving the sidewall passivation intact. After the bottom of the trench was cleared to the underlying Si handle wafer, XeF_2 was used to isotropically etch the handle Si, thus undercutting and releasing the features patterned in the device Si layer. The released device Si structures were not etched by the XeF_2 due to protection from the top SiO_2 mask, sidewall passivation, and the buried SiO_2 layer. Optimization of the XeF_2 process and the sidewall passivation layers will be discussed. The advantages of releasing SOI devices with XeF_2 include avoiding stiction, maintaining the integrity of the buried SiO_2, and simplifying the fabrication flow for thermally actuated devices. Sandia National Laboratories is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:20am **PS+MN-WeM5 SF_6/O_2/HBr Plasma Processes for the Etching of High Aspect Ratio through Silicon Via**, ***S. Avertin***, STMicroelectronics, France, *E. Pargon, T. Chevolleau*, Ltm - Umr 5129 Cnrs, France, *F. Leverd, P. Gouraud, C. Verove*, STMicroelectronics, France, *O. Joubert*, Ltm - Umr 5129 Cnrs, France

Today, the integration density and the chip dynamic power consumption are limiting and restricting phenomena. More than 50% of this consumption is due to long horizontal interconnects, and this rate is projected to increase. One solution to resolve these problems is 3D-Integration which provides smaller wire-length distribution by minimizing the connection length thanks to the fabrication of vertical vias through the silicon substrate or/and the chip. The ITRS roadmap requirement is to etch vias with 2-5 µm in diameter and high aspect ratio (>5). For deep silicon etching, the Bosch etch process which consists in alternating isotropic etching and deposition steps leads to the formation of the so-called scalloping phenomenon on the sidewalls (>100nm). In this paper, we propose to characterize and develop conventional plasma etching processes as an alternative to the Bosh process. The etching development is carried out in ICP reactor accepting 300mm wafers (DPSII from AMAT™) using SF_6/O_2/HBr plasma chemistries. The scientific objectives are to study the etching mechanism and passivation layer formation in order to get high etch rate ($>3\mu m.min^{-1}$), straight profiles and a controlled undercut (<50nm). The etching profiles and etch rates have been analysed using Scanning Electron Microscopy while etch and passivation mechanisms have been studied by quasi-in-situ X-ray Photoelectron Spectroscopy (XPS) and plasma diagnostics (Mass Spectroscopy, ion flux probe..). Preliminary results indicate that the etch mechanisms are strongly driven by the ratio of neutral over ion fluxes and that the etch process is very sensitive to microscopic effects such as the local loading of fluorine and oxygen radicals which is directly correlated to the local pattern density. Through a better understanding of the etch mechanisms, high aspect ratio silicon via with anisotropic profiles and minimized undercut have been obtained.

9:40am **PS+MN-WeM6 Study on the High Aspect Ratio Si Etch for D2x Devices**, ***Y. Gwangyong***, *P. Jongchul*, Samsung Electronics, Republic of Korea

As the design rule of the semiconductor devices decreases, the device fabrication technology is facing many difficulties. One of issues is the STI trench etching profile in case of the aspect ratio(A/R) over 20, and the traditional etching technology is not working properly any more. One among those problems is intra-cell loading which is due to the insufficient exhaustion of by-product from the narrow space (less than 30nm). The other is the bowing profile which results in the bad STI filling to generate the severe electrical short fails of a DRAM device. In this study, we researched and developed the innovative STI trench etching technologies to improve those problems. The one is the bias-pulsed plasma etching that repeats periodically plasma ON and OFF, which gave the dramatic decrease of the intra-cell loading. In addition that gave the side p assivation effect to result in straight side-slope without bowing. These two effects are due to the

byproduct exhaustion and the radical attaching during the plasma OFF time. A nd the high temperature etching process and the multi-step Oxygen flashing process also improved the intra-cell loading significantly. We got to know that these new Si etching technologies are successfully applied to the future high A/R(> 15:1) STI process for D2x DRAM devices.

10:40am **PS+MN-WeM9 Key Challenges in Extremely High-Aspect-Ratio Dielectrics Etching at 3x nm DRAM and Beyond**, ***S.K. Lee***, *J.-H. Sun, S.O. Lee, J.-S. Bang, S.-I. Lee, C.-M. Lim, S.-Y. Kim, D.-G. Lim, S.-K. Park, J.-G. Jung*, HYNIX Semiconductor Inc., Republic of Korea

11:00am **PS+MN-WeM10 Microstructures Etching on Silicon with the STiGer Process**, ***T. Tillocher***, GREMI, France, *J. Ladroue*, GREMI - STMicroelectronics, France, *F. Moro, G. Gommé, P. Lefaucheux*, GREMI, France, *M. Boufnichel*, STMicroelectronics, France, *P. Ranson, R. Dussart*, GREMI, France

The STiGer cryoetching process can be alternatively used to the Bosch process or the cryogenic process to etch high aspect ratio structures. It has been developed thanks to our knowledge of the passivation mechanisms in cryoetching. In the standard cryogenic process, patterned Si substrates cooled down to very low temperatures are exposed to continuous SF_6/O_2 plasmas. A SiO_xF_y-type passivation layer is formed on the sidewalls and prevents etching. This film has the property to desorb under ion bombardment or when the substrate is heated. We also showed that SiF_4/O_2 plasmas can be used to create or reinforce a passivation layer in cryogenic etching.

The STiGer process consists of cycling passivation steps (SiF_4/O_2 plasmas) and etching steps to get vertical structures. The etching steps can be either isotropic (SF_6 plasmas) or anisotropic (SF_6/O_2 plasmas). Like the cryogenic process, it is required to cool the Si substrate with liquid nitrogen.

The STiGer process combines advantages of both Bosch process and cryogenic process. Due to the cyclic passivation steps, the SiO_xF_y film is stronger than in "standard" cryoetching. In addition, the passivation layer desorbs when the substrate is heated back to room temperature. Thus, unlike the Bosch process, there is no need to clean the microstructures and the chamber walls after each process run. Moreover, the robustness is enhanced in comparison with "standard" cryoetching : the profiles are less sensitive to temperature variations.

But, like the standard cryogenic process, a cooling is required and like in Bosch etching, a scalloping is present on the sidewalls. However, it is possible to minimize this effect by tuning the etching and the deposition steps.

We will present our most recent performances with the STiGer process. Our objectives are to etch sub-micron trenches and holes that will be further used for the realization of integrated capacitors and Through Silicon Vias (TSV). But obviously, the STiGer process can be utilized for silicon micromachining in general.

Finally, we will see how such a process can amplify Columnar MicroStructures (CMS).

Plasma Science and Technology
Room: Aztec - Session PS-WeM

Plasma Surface Interactions (Fundamentals & Applications) I
Moderator: M. Hori, Nagoya University, Japan

8:00am **PS-WeM1 On the Mechanism of Plasma Surface Interactions in Electron Beam-Generated Plasma in Nitrogen Environment**, ***E.H. Lock***, *S.G. Walton, R.F. Fernsler*, Naval Research Laboratory

There are numerous features of electron beam-generated plasmas that distinguish them from discharges. In particular, most of the electron beam energy is spent on gas ionization (≈ 50 %), some on gas dissociation and very small amount on excitation. Thus, less radicals and photons are produced in electron beam-generated plasmas compared to discharges. Moreover, the electron temperature is low (< 1eV) so that the plasma potential is low and therefore the energy of the ions (1-5 eV) that attack the surface is low. These low ion energies minimize the undesirable physical sputtering and ion-assisted chemical etching of polymer surfaces, thereby limiting changes to the polymer *surface morphology* and the *depth of modification*. Despite these differences, the chemical structure of the polymer surface exposed to electron beam plasma is changed. In this work, we focus on understanding the mechanism of plasma induced polystyrene modification in nitrogen through a careful analysis of the functional groups formed and their distribution with depth.

This work was supported by the Office of Naval Research.

8:20am **PS-WeM2 Breakthrough of Compatibility between Bowing-free Profile and Bottom CD in High Aspect Ratio Dielectric Etch Using DC Superimposed Capacitively-Coupled Plasma**, ***A. Nakagawa***, *H. Mochiki, M. Dojun, K. Yatsuda, S. Okamoto*, Tokyo Electron AT Limited, Japan

Fabrication of latest DRAM capacitor structure requires precise etch profile control of silicon dioxide due to the continuous trend of narrowing pitch and high aspect ratio (HAR) features. While a number of issues are recognized such as twisting and bottom distortion, bowing became an outstanding subject for DRAM technology development for its complexity to cope with the bottom CD; even slight bowing leads to interference with the adjoining structures, and adjustment of process conditions frequently accompanies decreased bottom CD. In the present report we explore the effect of DC superimposition in capacitively-coupled plasma (CCP) as a countermeasure, taking advantage of its controllability on necking level at the mask facet.

Generally speaking, bowing is induced by the reflected ions at the mask facet attacking silicon dioxide sidewalls. Moreover, shrunk mask entrance interferes with incident radicals to transfer to the hole bottom, narrowing its size. One of the solutions utilizes high ion energy, but our results demonstrated a strong correlation between mask necking and bottom CD, thus the evaluation focused on optimization of mask necking.

Next, observation of deposition at the silicon dioxide sidewall varied with process parameters lead to systematic understandings of its physical amount and local enhancement, as well as the declining behavior at the removal process. By means of process parameters, the necking degree of the mask opening was controlled and the relationship among necking, bowing and bottom CD was examined.

As a result, it is necessary to improve necking at mask opening to minimize bowing and to keep bottom CD simultaneously. Optimization of process parameters enables etch profile enhancement by dispersing necking location, which normally decreases selectivity to mask. However, DC-superimposed CCP facilitated maintaining selectivity to mask with preferable etch profile, and less bowing with sufficient bottom CD.

8:40am **PS-WeM3 High Resolution Cryogenic Silicon Etch Process Development for Nanoscale Trenches**, ***Y. Wu***, Oxford Instruments, Lawrence Berkeley National Laboratory, *D. Olynick*, Lawrence Berkeley National Laboratory, *A. Goodyear*, Oxford Instruments, *C. Peroz*, Abeam Technologies, *S. Dhuey, X. Liang, S. Cabrini*, Lawrence Berkeley National Laboratory

We present work on the development of a cryogenic silicon etch process suitable for etching shallow and high aspect ratio nanoscale features below 50 nm for use in nanophotonics applications. With shrinking feature sizes, profile and critical dimension control tolerance is reduced and appropriate processes must be developed. Cryogenic silicon etching using SF_6-O_2 offers several advantages over fluorocarbon or heavier halogen based processes. For example, low bias voltages can be used, reducing mask erosion and ion damage. In addition, the etching process is not purely ion dependent which reduces some of the problems at small feature sizes associated with the ion angular distribution and ion interaction with the sidewall which can cause less than ideal profiles. Furthermore, sidewall contamination is minimal eliminating critical dimension (CD) variations due to etch residue cleaning. Two challenges to creating a suitable cryogenic SF_6-O_2 process for 50-100 nm features and below, is optimizing the passivant to eliminate undercut and reducing the etch rate enough to control the process. Furthermore, an etch process which changes in time accordingly to the etch depth and aspect ratio may be necessary for features below 20 nm.

The cryogenic SF_6-O_2 based silicon etching process was investigated in an Oxford Instruments ICP 380 using a L18 Taguchi design of experiments (DOE) matrix. For the DOE, trench type features sized 300-500 nm are investigated. Parameters varied include pressure, temperature, RF power, ICP power, He backing pressure, and oxygen content. The effects on the etch rate, selectivity, profile angle, and surface roughness were examined. The process was then finely tuned for etching of densely packed silicon trenches ranging from 100 to 10 nm. These features are patterned both with electron beam lithography and nano-imprint lithography techniques. Resist selectivity is high in both cases: from 10:1 to 20:1. Vertical and smooth sidewalls were obtained . Etched patterns were used to create nanophotonic devices such as nanospectrometers and laser waveguides and imprint masks for high resolution applications.

9:00am **PS-WeM4 Quantitative Analysis and Modeling of Dry Etch Induced Physical Damage in Si Surface Layer**, ***J.H. Yoon**, W.S. Kim, J.W. Han, D.H. Kim, J.Y. Lee, K.S. Shin, C.J. Kang*, Samsung Electronics, Republic of Korea

9:20am **PS-WeM5 On the Role of CF in Fluorocarbon Plasmas: Gas-Phase Reactions and Surface Interactions**, ***M.F. Cuddy**, E.R. Fisher*, Colorado State University

A complete understanding of the nature of fluorocarbon (FC) plasma systems necessarily includes a description of CF_x species behavior, including CF, CF_2, and CF_3. Our current research focuses primarily on understanding the gas-phase properties and reactions and gas-surface interactions of CF molecules produced from sparsely polymerizing CF_4 and C_2F_6 plasmas. An enriched understanding of these systems can elucidate the mechanisms contributing to film growth and may pave the way for enhanced plasma deposition and etching applications. To this end, we have employed laser induced fluorescence spectroscopy (LIF) and optical emission spectroscopy (OES) to probe the gas-phase behavior of CF, including calculations of rotational and vibrational temperatures. From these analyses, we determine that CF rotational states equilibrate with the plasma gas temperature at around 300 K. In addition, time-resolved actinometry has been employed to investigate gas-phase kinetics of the CF molecule as well as other CF_x species in a range of FC systems. We have also extended the LIF studies to our unique imaging of radicals interacting with surfaces (IRIS) technique which probes the gas-surface interface during plasma processing. CF species exhibit a surface gain in density, with surface scattering coefficients greater than unity for Si and ZrO_2 substrates, indicating production of the molecule at film-passivated surfaces. For comparison, IRIS results for CF_2 in the same plasmas will also be discussed. Surface analyses by high-resolution x-ray photoelectron spectroscopy (XPS) and variable angle spectroscopic ellipsometry along with the gas-phase data have culminated in a proposed mechanism for gas-surface interactions of these molecules during plasma processing of Si and ZrO_2 whereby the contributions of both CF and CF_2 molecules to film formation is summarily developed.

9:40am **PS-WeM6 "Designer" Ion Energy Distributions on Substrates Immersed in a Plasma**, ***P. Diomede**, D.J. Economou, V.M. Donnelly*, University of Houston

The energy of ions bombarding the substrate is critical in plasma etching (and deposition) of thin films. In conventional plasma processing, employing a sinusoidal substrate electrode voltage, the ion energy distribution (IED) is often very broad. However, as film dimensions approach the atomic level, control of the IED becomes critical. For example, selectivity considerations often dictate a narrow IED with a specified peak energy. In this work, semi-analytical models and particle-in-cell (PIC) simulations are employed to achieve "designer" IEDs, i.e., distributions with a desired shape and energy spread. This is accomplished by applying tailored voltage waveforms on the substrate electrode (spike, staircase, judiciously distorted square wave, etc.). Such waveforms can provide, for example, nearly mono-energetic IEDs or other desired shapes. Semi-analytic model results are compared with those of PIC simulation to identify the range of validity of the semi-analytic model. Predicted IEDs are also compared with experimental data under both collisional and collisionless sheath conditions. Strategies to control the energy flux of bombarding ions or to distribute the total energy flux to different energies will also be discussed.

Work supported by DoE Plasma Science Center and NSF.

10:40am **PS-WeM9 Modeling of Plasma-Induced Damage and Its Impacts on Parameter Variations in Advanced Electronic Devices**, ***K. Eriguchi***, Kyoto University, Japan **INVITED**

With scaling of advanced electronic devices, plasma-induced damage (PID) has been investigated extensively from various viewpoints. Although suppressing PID is one of the critical issues in plasma process optimization, there have been few reports which correlate the plasma parameters to device performance in terms of PID.

This study discusses one of the PID mechanisms, physical damage induced by ion bombardment on Si surface. We propose a new comprehensive framework linking an ion energy and the distribution function to device parameters, i.e., a unified PID design.[1] The framework is based on a modified range theory[2] and an analytical device-degradation model.[3,4] To verify the validity, we performed both experiments to clarify the damaged-layer structures (the thickness, defect site density, and the electrical properties) by novel techniques[5] and simulations (molecular dynamics and device simulations) to understand the quantitative effects.

We demonstrate prediction of performance degradation in metal-oxide-semiconductor field-effect transistors (MOSFETs) damaged by an inductively coupled plasma reactor which can apply the bias with two different frequencies (400 kHz and 13.56 MHz). The model prediction indicates that, in typical etching processes, the damaged-layer thickness can be determined primarily by an average self-dc-bias voltage rather than applied bias frequencies. This implication is found to be in good agreement with experimental results. Moreover, one can estimate also variation in device parameters from basic plasma parameters. Thus, it is concluded that the proposed framework is a key concept for future process and device designs.

1)K. Eriguchi et al., IEDM Tech. Dig. (2008) 443.

2)K. Eriguchi et al., to be published in Jpn. J. Appl. Phys., 2010.

3)K. Eriguchi et al., Proc. Symp. Dry Process (2009) 267.

4)K. Eriguchi et al., IEEE Electron Device Lett. 30, 1275 (2009).

5)K. Eriguchi et al., Jpn. J. Appl. Phys. 47 (2008) 2446.

11:20am **PS-WeM11 Time Resolved Diagnostics of a Pulsed Dual-Source Inductively Coupled Plasma**, ***H. Shin**, W. Zhu, X. Lin, V.M. Donnelly, D.J. Economou*, University of Houston

A novel dual-source inductively coupled plasma (ICP) system was designed and built to control the electron energy distribution function (EEDF) in the plasma, and the ion energy distribution (IED) on the substrate. The main ICP source has a Faraday shield to minimize the RF component of the plasma potential. The substrate electrode, as well as a "boundary" electrode in contact with the plasma, can be independently biased by DC or RF voltages, of the desired waveform, to influence the IED. A secondary tandem ICP source can inject plasma, radicals or metastable atoms to the main ICP to influence the EEDF. The main ICP source was characterized using a Langmuir probe (LP), trace rare gas optical emission spectroscopy (TRG-OES), and an electrostatic ion energy analyzer. Emphasis was placed on pulsed plasma operation to achieve better control of the IED (as well as the ion angular distribution). With the Faraday shield installed, the plasma potential was several volts lower, and the peak-to-peak RF voltage of the plasma potential was suppressed to 1-2 V, as compared to the case without Faraday shield, allowing for smaller spread of the IED. The plasma potential, and thus the peak of the IED could be precisely controlled by the voltage applied to the boundary electrode. Accurate control of the ion energy and width of the IED is important for processes such as atomic layer etching, for which the threshold energies between etching and sputtering differ by only several volts. During the OFF period of a square wave modulation of the plasma power (50 μs ON, 50 μs OFF), the electron temperature decayed from 3.1 eV to less than 0.25 eV, with only a 20 % drop in plasma density for a 10 mtorr pressure, 200 W (average) power argon plasma. Time resolved EEDFs were also measured by the LP and compared to those extracted from TRG-OES experiments during the ON and first few ms of the OFF time. Tailored voltage waveforms were used to obtain "designer" ion energy distributions on the substrate. Finally, results for other gases (such as krypton and oxygen) will be discussed and compared to those obtained for argon plasmas.

Work supported by the DoE Plasma Science Center and NSF

11:40am **PS-WeM12 Investigations on Physical Processes for Low Temperature Plasma Activated Wafer Bonding**, ***T. Plach**, K.H. Hingerl*, University of Linz, Austria, *D.V. Dragoi, G.M. Mittendorfer, W.M. Wimplinger*, EV Group, Austria

Direct wafer bonding is a "simple" method of directly connecting wafers, with suitable (in terms of micro-roughness and flatness) surfaces, permanently to each other, by bringing them into contact and subsequently annealing them. The conventional process for hydrophilic oxidized Silicon surfaces (native as well as thermal oxide) is well understood, and explained the following way:

Up to 100°C the substrate surfaces are held together via van der Waals interaction which is mediated by a few monolayers of water. In the range of 100-200°C the water diffuses away from the interface both along the interface and through the oxide into the crystalline bulk, where it reacts with the silicon and forms oxide. The increase of the bond strength from 50% to 100% of Si bulk strength is usually attributed to a closing of gaps at the interface [1], which starts at the softening temperature of the thermal oxide at around 850-900°C.

Low temperature plasma activated direct wafer bonding for a pair of native oxide – thermal oxide interfaces is a process that lowers the required annealing temperatures necessary for reaching high bond strength. Bulk strength can be realized by plasma activation with subsequent annealing at 300°C. At this temperature conventional wafer bonding reaches half of Si bulk strength, and is limited by gaps at the bonding interface. The mechanism behind this improvement compared to the non activated process is still under discussion.

To clarify the mechanism for this commercially available process, different bonding experiments were performed to evaluate the lifetime of the surface

activation and the achievable bond strength when using substrates with various orientations. Interfaces of bonded wafer pairs were investigated by transmission electron microscopy (TEM). TEM images clearly show that there is no discernible interface between the native oxide on one side and the thermal oxide on the other side.

By covering half of the wafer during plasma activation, comparisons between the activated and non-activated region could be made by atomic force microscopy, by spectroscopic ellipsometry, by Auger analysis and by X-ray photoelectron spectroscopy.

It was found that the top surface stoichiometry is chemically changed, which favors bonding. Finally a model for the mechanism that explains the experimental results will be presented.

[1] Q.-Y. Tong, U. Gösele, *Semiconductor Wafer Bonding: Science and Technology,* Wiley, (1998)

Plasma Science and Technology
Room: Aztec - Session PS1-WeA

Plasma Surface Interactions (Fundamentals & Applications) II
Moderator: J. Guha, Lam Research Corporation

2:00pm **PS1-WeA1 VUV-Induced Bond Scission and Site-Specific Nitridation in Organosilicate Glass: Bulk and Surface Effects**, ***S. Behera****, University of North Texas, *J. Lee,* University of California-Berkeley, *S. Gaddam, S. Pokharel,* University of North Texas, *D.B. Graves,* University of California-Berkeley, *J.A. Kelber*, University of North Texas

In-situ XPS and ex-situ FTIR have been used to characterized the effects of ionizing vacuum ultraviolet (VUV— 147 nm) photons on the surface composition of organosilicate glass (OSG; k = 3.0). VUV irradiation is an important component of the plasma environment, and both the types and kinetics of VUV- induced effects must be understood in order to accurately control and model plasma effects. Irradiation was carried out in vacuum (10^{-6} Torr), and in the presence of 10^{-4} Torr NH_3 so that NH_3 reactions with VUV-induced reactive sites would cause chemical shifts in XPS core level spectra, permitting a more detailed characterization of photo-induced chemistry. The effects of photo-excited gas phase species are negligible under these conditions, as confirmed by experiments with the light path parallel to the surface. FTIR and XPS data after photoirradiation in vacuum indicate photon-induced Si-C and Si-O bond scission. Lifetimes of bulk Si reactive sites are ~ 6 days, as determined by Si-OH, but ~ minutes at surface sites due to reaction with chamber ambient. Core level XPS spectra recorded after irradiation in the presence of NH_3 show similar effects, but with nitridation at Si sites, and not at carbon sites. Si-C/Si-O bond breaking and C-C bond formation obey first order kinetics. At longer exposure times, the nitridation process saturates while the Si-C/Si-O bond scission and C-C bond formation processes do not, consistent with photo-induced surface densification inhibiting NH_3 diffusion into the solid. However, similar increases in surface carbon intensity were observed for photoirradiation of SiO_2 with ~ 1 monolayer of surface carbon, indicating that reaction of background gases with surface reactive sites may also be a factor. Preferential Si-N bond formation and absence of C-N bond formation were also reported[1] for OSG bombardment by Ar^+ in the presence of NH_3 and suggest fundamentally different dissociation pathways/kinetics at Si vs. C sites created by either ion bombardment or ionizing photoirradiation. C-C and C-H bond dissociation enthalpies are larger than those of Si-H or Si-C bonds, but smaller than that of Si-O, so this site specificity is not readily explainable on the basis of bond strengths alone.

[1]J. A. Wilks and J. A. Kelber, Applied Surface Science **255** (2009) 9543

Acknowledgements: This research was supported by the Semiconductor Research Corporation under Task IDs 1862.001 and 1862.002.

2:20pm **PS1-WeA2 Real-time Measurements of Material Modifications by VUV Radiation during Plasma Etching of 193nm PR**, ***F. Weilnboeck***, *R. Bruce, G.S. Oehrlein,* University of Maryland, *T.-Y. Chung, D.B. Graves,* University of California, Berkeley, *M. Li, D. Wang,* Dow Electronic Materials, *E.A. Hudson*, Lam Research Corporation

Plasma radiation in the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral range is a fundamental component of plasma processes used for pattern transfer of nanometer structures. Photons in this wavelength range can lead to severe modification of photoresist (PR) materials in depths exceeding 100nm. We studied the material modifications of fully formulated 193nm PR by plasma photon radiation in Ar plasma discharges. A novel filter approach was applied allowing to probe PR surface modifications in real time by *in-situ* ellipsometry during plasma processing while protecting the PR against ion bombardment. Different filter materials enable to test dependencies on wavelength ranges of the plasma radiation from visible to VUV light. Material modifications were also characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. By combining these data with optical multilayer ellipsometric simulations, material thickness reduction and changes in optical properties could be understood on a molecular level.

Radiation in the UV/VUV spectral range was found to modify the PR at a depth of ~100nm leading to thickness reduction of up to 12nm, whereas radiation in the VIS spectral range modifies the entire film (~400nm) leading to marginal changes in the film thickness. The thickness reduction is caused by material loss, mainly by detachment and loss of lactone, and to a larger extent by densification of up to 9% following the detachment of the PR pendant groups.

Radiation exposure also leads to a change in film optical properties which is discussed in terms of a bond polarizability model. This enables correlation of the measured data with changes of the PR structure on a molecular level. For exposure of the PR to UV/VUV radiation it was found that besides loss of lactone and detachment of the PR pendant groups a significant amount of C-C bonds were lost which can be directly correlated to changes in the polymer structure by chain scissioning reactions.

Real time measurements allow for extracting the temporal evolution of material removal, densification and changes in film optical properties as a function of photon flux and degree of modification. It was found that material modification can be separated into two fundamentally different regimes. In the initial exposure period to plasma radiation in the UV/VUV spectral range changes in film properties are rapid and mainly limited by the photon flux. For extended exposure times modification is flux dependent but limited by the unmodified material remaining in the film after the initial exposure period.

2:40pm **PS1-WeA3 Deciding Factors for Line-Edge-Roughness (LER) Formation and Plasma-Resistance of ArF Photoresist during Plasma Etching Processes**, ***T. Uesugi***, *K. Koyama, B. Jinnai,* Tohoku University, Japan, *S. Maeda, K. Kato, A. Yasuda, H. Momose,* Mitsubishi Rayon Co., Ltd, Japan, *S. Samukawa*, Tohoku University, Japan

ArF excimer laser (193nm) lithography is used in the fabrication of sub-100-nm devices. However, during plasma etching processes, activated species radiated from plasma, such as ions, radicals, and photons, degrade ArF photoresist, resulting in low etching resistance and the formation of line-edge roughness (LER). To solve these issues, it is important to understand the interaction of plasma and ArF photoresist and to clarify deciding factors for the plasma resistance and the formation of LER in ArF photoresist. For this purpose, using our developed neutral beam process, effects of the activated species from plasma are divided into physical bombardment (by ions), chemical reactions (by radicals), and UV radiation. UV radiation drastically increased the etching rates of ArF photoresist films, and, in contrast, chemical reactions enhanced the formation of surface roughness in ArF photoresist. FTIR analysis shows that UV radiation preferentially dissociates C-H bonds in ArF photoresist, rather than C=O bonds, because of these bond dissociation energies; E(C-H, 4.25eV) < E(C=O, 7.71eV). This indicates that the etching rates of ArF photoresist are determined by UV radiation, because UV radiation can break C-H bonds, which are a majority of structures in ArF photoresist. On the other hand, according to the FTIR analysis, c hemical species, such as radicals and ions, are likely to react with C=O bonds, especially C=O bonds in lactone groups of ArF photoresist due to the structural and electronic effects of lactone groups. As a result, the etching rates of ArF photoresist can microscopically vary in different bond structures, leading in the enhancement of surface roughness in ArF photoresist. To reduce the chemical reactivity and the surface roughness, radical trap additives were injected into ArF photoresist. Radical trap additives, which can reduce surface roughness by 30%, are very effective to suppress the roughness formation in ArF photoresist.

3:00pm **PS1-WeA4 Smoothening of 193 Immersion Resist by 172 nm VUV Exposure**, ***E. Kunnen***, *A. Vaglio Pret,* IMEC, Belgium, *O. Luere,* CNRS-LTM, France, *L. Azarnouche,* STMicroelectronics, France, *E. Pargon,* CNRS-LTM, France, *P. Foubert, R. Gronheid, D. Shamiryan, M.R. Baklanov, W. Boullart*, IMEC, Belgium

At today's date 193 immersion lithography is used in semiconductor industry to print lines of less than 40nm half pitch, continuing the scaling. One of the challenges is to reduce line edge variations, or Line Width Roughness (LWR). It has already been pointed out earlier that LWR can be significantly reduced during the subsequent dry etch step. One of the important components acting on LWR during the dry etch is the VUV light emitted from the plasma, however, the exact mechanism is not yet revealed.

The photoresist pattern profile and its chemical modifications are studied as a function of VUV dose. A 172 nm Xe_2* excimer 30mW/cm^2 light source is used to expose patterned and blanket (resist & organic BARC) wafers, exposing them from 2 to 256 seconds under nitrogen ambient and controlling the temperature within 2°C. SEM-CD top-down image analysis gives us spatial and information in both spatial and frequency domain through Critical dimension (CD), CD-Uniformity, LWR and Power Spectr al Density (PSD). Three dimensional information is recorded by CD AFM measurements. The thickness, refractive index and extinction coefficient are deduced from spectral ellipsometric (SE) measurements. Mass measurements provide density. Fourier Transformed Infrared Spectroscopy

* Coburn & Winters Student Award Finalist

(FTIR) analyses provide information on the molecular bonds. Finally, chemical analysis will be performed by elastic recoil detection (ERD) and Time of flight secondary ion mass spectrometry (TOFSIMS).

Significant changes in CD and LWR are observed up to 12s (360 mJ/cm^2) of VUV exposure time corresponding to a dose of about 1 photon per atom. For higher exposures the integrity of the lines deteriorates compromising the accuracy in the SEM-CD analyses. Initially, CD and LWR decreases while the correlation length increases. PSD analysis shows that the reduction is attributed to a decrease in the high frequency roughness region. For longer exposure, a CD increase is observed and finally low frequency roughness increases, the total LWR. The CD evaluation indicates a resist reflow that is driven by surface tension towards a more rounded shape. Mass and thickness measurements over the whole exposure range show a decrease that goes linearly with the logarithm of the exposure time, while density remains about constant. FTIR indicate a correlation of the observed changes with the removal of the lactone bonds at 1800 cm-1.

In conclusion the dose range at which VUV impacts LWR is measured to be around 1 photon/atom. Initially a CD and LWR decrease is observed while for larger doses the trend is the opposite. Change of mass and thickness follows a first order kinetic equation, which is quite typical for simple desorption processes.

4:00pm **PS1-WeA7 Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Surface Roughening: the Dependence on Polymer Structure***, **T.-Y. Chung**, D.B. Graves,* University of California, Berkeley*, F. Weilnboeck, G.S. Oehrlein,* University of Maryland*, E.A. Hudson,* Lam Research Corporation*, M. Li*, The Dow Chemical Company

Previous vacuum beam studies showed that methacrylate-based 193 nm photoresist (PR) will roughen due to the synergistic effects of ion bombardment, vacuum ultraviolet (VUV) photon and substrate heating [1]. The surface roughness and surface morphology is similar to that after inductively coupled argon plasma exposure under similar ion and VUV fluences and energies [2]. However, 193 nm PR is a heteropolymer, with three separate side-groups that could be photolyzed due to the plasma-generated VUV, and this could complicate analysis of roughening mechanisms. We therefore examined several associated homopolymers to better understand the role of the side groups in roughening under plasma exposure. We chose two homopolymers: 2-methyl-2-adamantyl methacrylate (MAMA, leaving group) and R-functionalized adamantly methacrylate (RAMA, polar group). At a substrate temperature of 65˚C, MAMA undergoes considerable loss of material under VUV-only exposure. In addition to the loss of CH2/CH3, C=O and C-O-C bonds in the polymer bulk observed by transmission Fourier transform infrared (FTIR) spectroscopy, mass spectroscopy analysis shows that the adamantane leaving group is lost from the film. In contrast, RAMA is relative insensitive to VUV irradiation. After simultaneous ion/VUV exposure at a substrate temperature of 65˚C, MAMA shows very high surface roughness while RAMA shows little surface roughening. The surface of MAMA is also significantly rougher than that of 193 nm PR processed under the same condition. It therefore appears that the leaving group in 193 nm PR, designed to cleave in the presence of photoacid during lithographic exposure and post-exposure bake, is the primary cause of 193 nm PR roughening, when combined with energetic ion bombardment, VUV irradiation and elevated heating.

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4:20pm **PS1-WeA8 Polymer Surface Modification: Vibrational Sum Frequency Generation Study for Plasma Etching***, **K. Ishikawa**, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

A comprehensive understanding of interaction between plasmas and nano-materials is essential for advanced plasma processing technology. By means of plasma-beams apparatus, complicated processes are expectedly convolved individual contributions such as ion, radical, and photons. The vibrational sum-frequency-generation (SFG) is a beneficial tool for addressing best sensitivity at surface and interface, breaking their centro-symmetry[1]. In this study, we have investigated polymer surfaces exposed to the plasma-beams by using SFG.

Samples used were spin-on methyl-siloxane polymer, which is able to used as low-dielectric-constants (Low-k) film for interconnects. Hydrophobic property exhibits since methyl end group, $-CH_3$, is terminated at end on siloxane.

Plasma beams, which directly extracted from a argon plasma by acceleration between 100 and 400 eV, were irradiated.

The SFG spectroscopy setup consists of a 1064 nm Nd:YAG laser, and optical systems, which create both visible (532 nm) and tunable infrared (1000-4000 cm^{-1}) radiations (Ekspla). The SFG spectra taken were decomposed into individually spectral features by fitting spectra calculated to that measured. Intensity of SFG signal emitted from the surface is phenomenogically expressed as the summation of non-resonant susceptibility and damped Lorentian oscillators, which are characterized by phases, strength, resonant, and damping wavenumber.[2]

Before plasma exposure, peaks at ~2930 and ~2970 cm^{-1} are arisen from C-H stretch of Si-CH_3. This strength coincides with that for a peak at around 1275 cm^{-1} in infrared spectra. After plasma exposure, surface methyl group is disappeared. At the present, it was interpreted that at early stage under ion irradiation, hydrogen is released from the end-on methyl group to create surface radicals, namely rupture of chemical bonds to methyl group is essential for elimination from end-groups on the surface.[3] Further detailed considerations should be conducted.

The surface modifications of plasmas have been studied by using the plasma-beam apparatus and the SFG spectroscopy. The end-groups of the polymer surface were changed only physical ion bombardments. To understanding surface chemical reactions and physical properties, nano- and atom- scaled views of not only bulk materials but also surface end-groups are informative.

Acknowledgments

This study was partly supported by the Tokai region knowledge cluster, Aichi Science and Technology Foundation.

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4:40pm **PS1-WeA9 Plasma-induced Mechanical Degradation of Silicon Microcantilever***, **C.H. Huang**, M. Tomura, Y. Yoshida, T. Ono,* Tohoku University, Japan*, S. Yamasaki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*, S. Samukawa*, Tohoku University, Japan

Miniaturization of microcantilever realized increasing resonant frequency and achieving high resolution in image sensing devices such as scanning probe microscopy. Thin film deposition and etching are widely used in micro fabrication process. Therefore, it is indispensible to use plasma process. However, the plasma process usually generates defects in the micro structure due to the high-energy ion bombardment, charge build-up and UV photon radiation from the plasma, which might degrade the mechanical characteristics of the micro elements, such as microcantilever, and result in MEMS malfunction.

In this study, a Si microcantilever was adopted to investigate the influence of plasma irradiation to mechanical characteristic. The Si microcantilever was fabricated with silicon on insulator wafer. After the fabrication, the microcantilevers were irradiated by inductively coupled plasma and neutral beam (NB) with argon gas at room temperature. The influences of the plasma and NB irradiations on Si microcantilevers were evaluated with Q factor and resonant frequency (f) using laser Doppler vibrometer before and after irradiation. After plasma irradiation, Q factor ratio [Q factor after irradiation/Q factor before irradiation] and f ratio [f factor after irradiation/f factor before irradiation] drastically decreased. The Q factor ratio didn't depend on the irradiation time and the f ratio decreased as the plasma irradiation time increased. On the other hand, the Q factor ratio and f ratio only slightly decreased after Ar NB irradiation, which indicates that NB process have great potential for MEMS application. To understand the degradation mechanism of Si microcantilever, defect (E' center) density on microcantilever surface was measured by electron spin resonance. The defect density increased when plasma irradiation time increased. The Young's modulus (E) of microcantilever calculated from f suddenly decreased and became plateau when E' center was over a threshold defect density. The Q ratio decreased when the microcantilever thickness decreased. It is because the ratio of defect depth to microcantilever thickness being higher. Given these results, plasma irradiation degrades the E resulting in the variation of the f. D egradation of Q factor is determined by the ratio of defect depth to microcantilever thickness.

5:00pm **PS1-WeA10 Gas-phase Diagnostics for Understanding Plasma Processing to Tailor the Surfaces of Inorganic Thin Films and Nanoparticles***, K.J. Trevino, S.M. Thagard, J.C. Shearer, J.M. Stillahn,* ***E.R. Fisher***, Colorado State University

Plasma-enhanced chemical vapor deposition (PECVD), plasma etching, and plasma modification of surfaces are emerging as important tools in the development of biomaterials, hard coatings and other diverse applications. Recently, we have explored the use of both low-pressure rf plasmas as well

as atmospheric plasmas to specifically tailor the surface properties of a variety of inorganic materials with a range of morphologies from flat substrates to membranes and nanoparticle systems. Despite the broad range of applicability of plasma processing for producing materials with specific surface properties (e.g. hydrophilicity, chemical functionality, etc.), many mechanistic details remain unknown. Understanding the contributions of gas-phase species is critical to understanding the chemistry that leads to specific surface modifications. In addition, the surface interactions of gas-phase plasma species provide critical molecular level information about plasma processing, especially at interfaces. In addition, power dissipation and energetics are also important for elucidation of mechanistic details in plasmas. The imaging of radicals interacting with surfaces (IRIS) technique uses laser-induced fluorescence (LIF) to provide spatially-resolved images of plasma species. Furthermore, IRIS provides direct information on the energetics of plasma-generated radicals as well as for species scattering off of surfaces. Combined with quantitative optical emission spectroscopy (OES) data, we have measured the internal and translational temperatures for a range of species in a variety of plasma environments. This work concentrates on OH radicals in H_2O plasmas used to create hydrophilic metal oxide surfaces, CH radicals in plasma polymerization systems for nanocomposite materials, and, SO_2 and CF_x species in dielectric etching systems. For many of these molecules, vibrational temperatures are significantly higher than rotational temperatures and the partitioning of energy is correlated to surface reactivity. Comparison between atmospheric and low temperature plasmas as well as flat vs. nanostructured substrates will be made. Preliminary results from computational models of our plasma systems will also be presented. The gas-phase data are complemented by a range of surface and materials analysis data that reveal a more detailed picture of the overall plasma process in each system.

5:20pm **PS1-WeA11 Wet SiO_2 Etch Rate Enhancement Due To Surface Fluorination By A Remote O_2/CF_4 Plasma**, ***D.L. Gilbert***, Mattson Technology Singapore PTE LTD

High Dose Implantation (HDI) for source/drain (S/D) is one of the critical steps for transistor formation. It becomes more complicated due to S/D junctions are designed to be shallower at proportional scaling down of the entire transistor. The photo resist (PR) mask is exposed to increasing number of implant species, higher dosages and energy levels. The top layer of the PR transforms to hard and cross-linked crust. Meanwhile, the sidewall of the PR mask collects a lot of spattered substrate (inorganic) materials. As a consequence, HDI photo resist strip (HDIS) is increasingly difficult to get residue free with controlled material loss and growth as required at lower node. One of widely used HDIS process solutions is remote O_2/CF_4 plasma followed by a wet chemical clean, such as dilute HF and/or SC1 solutions. However, these strip / clean processes also attack the underlying SiO2 films. It is critical to control such SiO2 loss for future IC production, as device sizes shrink. Therefore, a delicate balance is to be discovered between effectively cleaning the wafer surface and etching into the SiO2 substrate. This paper discusses the significant synergy between the O_2/CF_4 processes and subsequent wet clean. It has been observed that the overall oxide removal through combined O_2/CF_4 dry clean and wet chemical clean is significantly higher than the sum of the independent oxide loss through dry clean and wet clean. The effect on CF_4 concentration in the plasma, O_2/CF_4 processing time, and temperature on the wet etch rate enhancement are explored. In an effort to reduce the etch rate enhancement, several post O_2/CF_4 processes such as a O_2 only plasma, a forming gas plasma, and a simple water rinse are employed. Results show that the oxide loss enhancement is due to the presence of a highly fluorinated surface post O_2/CF_4 dry clean. This fluorinated oxide surface readily dissolves in wet etch chemistries. Furthermore, once desorbed from the wafer surface, the fluorine may increase the local concentration of species responsible for etching oxide films.

Plasma Science and Technology
Room: Galisteo - Session PS2-WeA

Neutral Beam Processing
Moderator: J. Joo, Kunsan National University, Republic of Korea

2:00pm **PS2-WeA1 Possible Applications of Neutral Beam Generated by Low Angle Reflection of a Reactive Ion Beam to Nanoscale Semiconductor Processing**, ***G.Y. Yeom***, Sungkyunkwan University, Republic of Korea **INVITED**

2:40pm **PS2-WeA3 Numerical Simulation of Neutral Beam Generation by Quantum Electrons Dynamics**, ***N. Watanabe***, *S. Ohtsuka, T. Iwasaki, K. Ono,* Mizuho Information & Research Institute, Inc., Japan*, Y. Iriye, O. Nukaga, S. Ueki, T. Kubota, M. Sugiyama,* BEANS Project 3D BEANS Center and University of Tokyo, Japan*, S. Samukawa*, BEANS Project 3D BEANS Center and Tohoku University, Japan

We have developed numerical simulation method which analyses neutral beam generated by collisions with aperture sidewalls.

The neutral-beam etching system developed by Samukawa, et al [1] has a carbon plate which has numerous apertures, where positive or negative ions pass through. In this system, we had found experimentally that most of those ions passing through the apertures are efficiently converted into neutral atoms with maintaining the motion energy. We consider ions are neutralized by the collision with aperture sidewall, namely, a negative ion transfers some of their valence electrons to the aperture sidewall by the collision, on the other hand, a positive ion receives some valence electrons from the aperture sidewall.

To realize more efficient neutral-beam etching system, we have to understand the dynamical process of electron transfer by the collision. The process of electron transfers can be described by the Quantum Mechanics as a time-evolution of wavefunction during the collision. For this purpose, we have developed computational simulation software named QuickQD[2,3] which can calculate the time-evolution of wavefunction of electrons around both an ion and the carbon plate during the whole process of collision. QuickQD is based on the density functional theory, and it can calculate the time-evolution of wavefunctions stably and efficiently.

Our numerical model consists of an ion and several carbon atoms forming a graphite sheet. We have taken the following ions and neutral atoms as the colliding ion respectively; Cl-, Cl, Cl+, Cl2-, Cl2, and Cl2+.

We have performed the numerical simulation of the collision of each ion and the carbon sheet. QuickQD has calculated the time-evolution of several ten wavefunctions of both the ion and carbon atoms. During the time-evolution, the ion has been moved to collide with the graphite sheet and then bounce back to its original position. At the end of time-evolution, we have counted the electron distribution left around the ion, and have estimated the valence number of the ion after the collision. In this way, we have determined the probability of neutralization of each ion. We have obtained results which show a Cl- is converted into Cl with a high probability, meanwhile a Cl2+ is converted into a Cl2 with a low probability. These numerical results agree well with the experimental results. We have established a numerical method that analyzes the neutralization process based on the Quantum Electrons Dynamics.

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3:00pm **PS2-WeA4 Development of a Defect-Free GaAs/AlGaAs Heterostructure Etching Process Utilizing Chlorine and Argon Mixed Neutral Beam**, ***X.Y. Wang***, *C.H. Huang, Y. Ohno, M. Igarashi,* Tohoku University, Japan*, A. Murayama,* Hokkaido University, Japan*, S. Samukawa*, Tohoku University, Japan

Dry etching is a key technique in top-down process for the fabrication of GaAs/AlGaAs nanometer-scale heterostructures such as quantum wire and quantum dot. For nanostructures, surface condition would affect the quantum-effect substantially. Therefore, it is important to suppress the effect of dry etching process by defect-free, atomically smooth etching profile, and control of etching selectivity. Plasma dry etching such as reactive ion etching process induces the etched defect since it has high energy ultraviolet (UV) photon irradiation and charged particles. The etched defect would reduce the optical and electrical properties of semiconductor materials. Alternatively, neutral beam has great potential for developing a defect-free dry etching process by its characteristics of completely suppressing UV photon irradiation and only generating the low energy neutral beam (below 100eV). In this work, we study on a $GaAs/Al_{0.3}Ga_{0.7}As$

heterostructure etching process by neutral beam etching with chlorine and argon mixed etching gas. The effect of different mixed ratio of chlorine and argon has been investigated. The results shows when 100% chlorine neutral beam used, the etching grass formation was observed on etched surface. To increase the argon mixed ratio in etched gas, the grass was eliminated and the etched surface roughness was smoother. As the best we know until now, when the 22% chlorine and 78% argon of mixed etched gas used, both the root-mean-square (rms) etched surface roughnesses of GaAs and $Al_{0.3}Ga_{0.7}As$ are about 0.6 nm (the rms surface roughness of as-received sample is about 0.4nm). Meanwhile, the etching rate of GaAs and $Al_{0.3}Ga_{0.7}As$ are 16 nm/min and 17 nm/min, respectively. It means the etching selectivity of $GaAs/Al_{0.3}Ga_{0.7}As$ is about 0.94. Additionally, to verify the defect-free property of neutral beam etching, the cross-section of etched GaAs etched profile was analyzed by transmission electron microscopy. The result shows that no crystalline defect can be observed at the top region of etched surface. In summary, we developed a promising dry etching process for nanometer-scale $GaAs/Al_{0.3}Ga_{0.7}As$ heterostructure with defect-free, etching selectivity of $GaAs/Al_{0.3}Ga_{0.7}As$ closes to 1, and atomically smooth etching surface roughness.

4:00pm **PS2-WeA7 Development of Sputter and CVD using the Hyperthermal Neutral Beam**, ***B.J. Lee***, *S.W. Choi, D.C. Kim, J.S. Kim, K.S. Oh, S.J. Yoo,* National Fusion Research Institute, Republic of Korea, *J.N. Jang, Y.J. Lee, M.P. Hong,* Korea University, Republic of Korea, *Y.C. Park*, Handong Global University, Republic of Korea

New deposition processes using Hyperthermal Neutral Beam, which has energy between 1 ~ 100 eV, have been developed for the damage-free deposition below 80 °C. Many studies concerning the plasma and heat damage problems during the deposition of transconductive oxide such as Indium Tin Oxide (ITO) on various organic materials which are vulnerable to those damages. This presentation discusses characteristics of ITO thin films deposited by brand-new plasma-damage - free sputtering process on cross-linked Poly 4-vinylphenol (PVP) layer at the room temperature using HNB. Nano-crystal (nc) Si TFT manufactured at low temperature (< 100 °C), namely CVD using HNB to satisfy the stability, V_{th} Shift, mobility and on/off ratio for OLED operation is also discussed. Very thin (< 5 nm) incubation layer for the transition from amorphous to crystal occurred while growing the nc-Si thin film on the glass was grown.

4:20pm **PS2-WeA8 Silicon Etching using Large Diameter Neutral Beam Source**, ***T. Kubota,*** BEANS Project 3D BEANS Center and University of Tokyo, Japan, *S. Ueki,* BEANS Project 3D BEANS Center, Japan, *O. Nukaga, M. Sugiyama,* BEANS Project 3D BEANS Center and University of Tokyo, Japan, *H. Ohtake,* Tohoku University, Japan, *S. Samukawa*, BEANS Project 3D BEANS Center and Tohoku University, Japan

Plasma etching is widely used for fabricating semiconductor electronic devices, microelectomechanical systems (MEMS), but plasma etching is known to cause damages due to the charge-up and UV irradiation. To overcome plasma-induced damages, neutral beam is widely studied by several groups in the world. Samukawa proposed a neutral beam source using negative ions in plasma and carbon aperture plate for neutralization [S. Samukawa, K. Sakamoto, and K. Ichiki, Jpn. J. Appl. Phys., 40, L779 (2001)]. The neutral beam source achieved high neutralization efficiency by using negative ions from pulse-time modulation plasma, and UV irradiation was drastically reduced. To apply this neutral beam source to mass production, we developed a large-diameter neutral beam source by using an 8-inch-diameter inductively coupled plasma etcher (Panasonic Factory Solutions Co., Ltd. E620) as an ion source. We measured flux and energy of neutral particles, ions, and photons and it was revealed that an argon neutral beam flux of more than 1 mA/cm^2 in the equivalent current density and a neutralization efficiency of more than 99%. Spatial uniformity of the neutral beam flux was within ±6%. Si etching with vertical profile using an F_2-based neutral beam was achieved with a high etch rate of about 100 nm/min. The spatial uniformity of the etch rate was better than ±5%. The etch rate was increased by applying bias power to the neutralization aperture plate, demonstrating that an accelerated neutral beam was successful in operation. This neutral beam source will enable the usage of damage-free neutral beam processes for practical use in the near future. A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO). This work is partly supported by Formation of Innovation Center for Fusion of Advanced Technologies, Special Coordination Funds for Promoting Science and Technology, Ministry of Education, Culture, Sports, Science and Technology.

4:40pm **PS2-WeA9 Microwave Plasma Source for the High Flux Hyperthermal Neutral Beam**, *B.J. Lee,* ***H.J. You****, S.W. Jang, Y.H. Jung, D.W. Kim, M. Koo,* National Fusion Research Institute, Republic of Korea, *Y.C. Park, J.T. Kim*, Handong Global University, Republic of Korea

In order to incident the high flux of Hyperthermal Neutral Beam (HNB) on the substrate the high plasma density and the shortest distance between the reflector, which converts ions to neutrals, namely neutralizer, and the substrate are required. ECR plasma source can both requirements. This presentation shows the features of ECR plasmas due to the Lisitano antenna, the vertical slotted antenna (VSLAN), the incline slotted antenna (ISLAN), and the rectangular slotted antenna (RESLAN) for the scanning type CVD. The characteristics of HNB Cu sputter for the Cu seed layer for Cu interconnect line of semiconductor as an application of plasma source from Lisitano antenna and HNB Al sputter for the thin film deposition of Al_2O_3 as one from RESLAN are also presented.

5:00pm **PS2-WeA10 Low Temperature, Lattice-plane-free, Anisotropic and Damage-free Oxidation by Neutral Beam Technology**, ***A. Wada,*** Tohoku University, Japan, *K. Endo, M. Masahara, S. Yamasaki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan, *S. Samukawa*, Tohoku University, Japan

To fabricate a metal-oxide-semiconductor field-effect transistor (MOSFET) with a three-dimensional (3D) structure several problems arise in the conventional thermal oxidation process, such as high temperature, the dependence of the oxidation rate on the lattice plane of silicon (Si) and non-oriented oxidation process. After high temperature processing, compression stress remains in the SiO_2 film due to the difference in thermal expansion coefficient between the Si substrate and SiO_2 film. The compression results in defects in the SiO_2 film, which leads to increased leakage current. Furthermore, in the case of gate oxidation in the fabrication of 3D MOSFETs, the oxide film on a 3D structure and substrate is not consistent due to the different oxidation rates resulting from different lattice planes between them, which cause a concentration of the electric field and dielectric breakdown. Moreover, conventional thermal oxidation (TO) process is non-oriented oxidation process which forms oxide film on whole Si surface, and hence, it is difficult to independently control the thickness of the dual-gate dielectric film such as a four-terminal FinFET. To overcome these problems, we propose low-temperature (< 300ºC) damage-free neutral beam oxidation (NBO) as an alternative oxidation process. We found that oxide film grown by NBO (NBO film) even at a low substrate temperature (300 ºC) exhibits performance characteristics of a gate dielectric film that are as high as that of thermal oxide film in terms of the relationship between equivalent oxide thickness (EOT) and leakage current. This is because beam-induced oxidation plays a dominant role in the formation of NBO films by bombardment with an oxygen neutral beam. Also, the oxidation rate of NBO is independent of the lattice plane of silicon, and the oxidation is anisotropic. Therefore, oxide film grown by NBO is advantageous in that it can be applied to a gate dielectric film for a 3D fin structure of MOSFET.

5:20pm **PS2-WeA11 Structure-designable Method to form Super low-*k* SiOC Film by Neutral-Beam-Enhanced Chemical Vapour Deposition**, ***T. Sasaki****, S. Yasuhara,* Tohoku University, Japan, *T. Shimayama, K. Tajima, H. Yano, S. Kadomura, M. Yoshimaru, N. Matsunaga,* Semiconductor Technology Academic Research Center (STARC), Japan, *S. Samukawa*, Tohoku University, Japan

To precisely control the dielectric constant and the structure of a low-*k* SiOC film, we have developed a neutral-beam-enhanced chemical vapour deposition (NBECVD) method. Using Ar NBECVD with precursors of methyl trimethoxy silane (MTMOS), dimethyl-dimethoxy-silane (DMDMOS), and dimethoxy-tetramethyl-disiloxine (DMOTMDS), we can precisely control the dielectric constant and the film modulus of low-*k* SiOC deposited on Si substrates because this method avoids precursor dissociation that results from electron collisions and UV photons in plasma. Optimizing the ratio between Si–O and Si–(CH3)*x* as well as the proportions of linear (two-dimensional SiOC), network and cage (three-dimensional SiOC) structures by changing the precursor and neutral beam energy, we obtained a *k* value of less than 1.9 and a reasonable modulus of more than 4GPa with an extremely water resistant and very thermally stable

.

Additionally, we investigated the resistance of the NBECVD low-*k* SiOCH to plasma-irradiation damage in comparison with conventional plasma CVD (PECVD) techniques. We found that the durability of a low-*k* SiOCH film structure to plasma irradiation strongly depended on the kind of Si–O structure the film had. In particular, a linear Si–O structure was less affected by plasma exposure than were network/cage Si–O structures. In addition, this linear Si–O structure helped to reduce the number of methyl groups removed from the film by plasma irradiation, which preserved the dielectric constant. Since the NBECVD technique can generate a low-*k* SiOCH film with more linear Si–O structures than conventional plasma CVD, the NBECVD film has very strong plasma durability.

Plasma Science and Technology
Room: Galisteo - Session PS+TF-ThM

Plasma Deposition and Plasma Enhanced ALD
Moderator: M. Shiratani, Kyushu University, Japan

8:00am **PS+TF-ThM1 High Rate Synthesis of Crystalline Si Film by Control of High Density Radicals with Dual Frequency PECVD**, ***J.G. Han***, *Y.S. Choi, Y.J. Kim, I.S. Choi*, Sungkyunkwan University, Republic of Korea **INVITED**

One of prime hurdle for high efficiency and cost effective Si film solar cell is enhancement of deposition rate of crystalline Si film with low defects at least higher than 1.0 nm/sec for cost effective solar cell device manufacturing. Crystalline Si thin films are synthesized at low temperature less than 350 ºC on glass by various dual frequency plasma CVD utilizing dual power inputs in a frequency range of RF to UHF. The deposition rate of crystalline Si film is significantly enhanced in a range of 0.8 nm/s to 2.0 nm/s by RF plasma CVD using SiH4 and H2 gas mixture with additional power input of very high frequency (VHF) and ultra high frequency (UHF). The volume ratio of crystalline and amorphous Si film structure is also controlled in a range of 45 % to 70 % with change of dual frequency power inputs and partial pressure ratio of SiH4 and H2. The significant improvement of deposition rate with additional power input of VHF and UHF is closely associated with enhanced generation of SiHx radicals from SiH4 molecules due to the secondary high density plasma generated by additional high excitation frequency. Hydrogen radical which contribute the formation of crystalline Si film with surface diffusion and chemical annealing is also generated intensively. This paper illustrates the results of change of deposition rate as well as microstructure with variation of duel power inputs and process parameters. The corresponding mechanism is discussed with plasma diagnostic data of silane and hydrogen radicals using optical emission spectroscopy (OES), Langmuir probe and radical monitors.

8:40am **PS+TF-ThM3 Room Temperature PECVD Synthesis of Hybrid Organic-Inorganic Nanolaminates**, ***R. Patel***, *C.A. Wolden*, Colorado School of Mines

Nanolaminates enable a new class of optoelectronic structures that are ultra lightweight, dimensionally stable, and have low cost with increased durability and flexibility. They are integral components in various applications serving as advanced dielectrics, flexible barrier coatings, and as optical components. In this work plasma enhanced chemical vapor deposition (PECVD) is employed to deposit functional polymer thin films on flexible substrates in order to make hybrid organic-inorganic nanolaminates for the applications described above.

Silicone-like coatings were deposited using hexamethyldisiloxane (HMDSO) and oxygen as precursors at room temperature. Film composition was assessed by spectroscopic ellipsometry and FTIR. A wide range of coatings, from inorganic SiO2-like films to flexible polymeric films could be deposited by appropriate control of parameters including the O2/HMDSO ratio, rf power, and working pressure. In this work we report on how these variables impact deposition rate, film composition, and nanolaminate performance. Growth rates as high as 100 nm/min were obtained, and crack free silica and polymeric films have been deposited on polyethylene.

For the production of organic-inorganic nanolaminates, two approaches were used for the formation of the inorganic layer. In one case HMDSO was used for deposition of both the silicone- and silica-like layers. In this case, the flowrate of HMDSO was held constant while other variables (power/O2 flowrate) were adjusted. In the second case, the inorganic layer was aluminum oxide that was formed using tri-methyl aluminum (TMA) and oxygen at room temperature. Self-limiting growth of alumina (~Å/pulse) was achieved by both plasma-enhanced ALD and pulsed PECVD. No impurities were detected in Al2O3 by FTIR by either technique under optimum conditions. Nanolaminates were constructed as a function of dyad composition and total number of dyads. In this paper we compare the performance of these various nanolaminates with respect to metrics such as adhesion and barrier properties.

9:00am **PS+TF-ThM4 Role of PEALD System Plasma Source Operation on Substrate Ion Bombardment and the Impact on HfO_2 and TiN Film Properties**, ***M.J. Sowa***, *G.M. Sundaram, E.W. Deguns, R. Bhatia, M.J. Dalberth, A. Bertuch, G. Liu, J.S. Becker*, Cambridge NanoTech, Inc.

Plasma enhanced atomic layer deposition (PEALD) has seen increased interest in recent years. Replacing one of the half cycles of the ALD process with a plasma generated radical dose has been successfully demonstrated to improve film electrical properties, improve deposition rates, enable lower temperature processing, and enable the use of precursors unsuitable for thermal processes. It is typically advantageous to operate the plasma source of PEALD systems in a “remote” mode, such that the substrate being processed does not have any exposure to energetic charged species. Rather, the longer-lived radicals generated in the remote plasma source react with the chemisorbed precursor from the previous half-cycle to form the desired film. Exposure of the substrate to energetic ion bombardment during the plasma half cycle has been demonstrated to lead to decomposition of the chemisorbed precursor which gives thick, non-uniform films with poor electrical properties. We have observed that, depending on the processing conditions utilized for generating the plasma, the plasma may be confined to the remote plasma source or may extend into the ALD processing reactor to varying degrees. The remote plasma source on our system is an inductively coupled plasma design consisting of a cylindrical quartz tube surrounded by a water-cooled copper inductor. We have investigated the quality of HfO_2 and TiN films grown in our PEALD system with various, controlled levels of substrate ion bombardment. Up to 300W of 13.56MHz rf is coupled to the copper inductor through an L-type matching network. Plasma gas mixtures of Ar with commonly used PEALD gases, O_2 or N_2, over a wide range of flow rates and pressures were investigated. We have quantified the encroachment of the plasma into the ALD reactor through the placement of Langmuir probes on the surface of a 200mm substrate which is placed onto the heated substrate holder of our PEALD system. We then deposited films of HfO_2 with tetrakis(dimethylamino)hafnium and Ar/O_2 plasmas and TiN with tetrakis(dimethylamino)titanium and Ar/N_2 plasmas at various levels of substrate surface bombardment. Resulting films were evaluated for stoichiometry, impurities, crystallinity, and relevant electrical properties including dielectric constant and leakage current for the HfO_2 and resistivity for the TiN.

9:20am **PS+TF-ThM5 HfTiSiON Film Growth by N_2 Plasma Exposure to Hf-Ti Liquid Nano Particles on SiO_2/Si**, ***T. Kitajima***, *T. Nakano*, National Defense Academy, Japan, *T.M. Makabe*, Keio University, Japan

1. Introduction

HfSiON is the most applicable chemistry for the high-k gate dielectrics with proper energy band alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO_2 utilizing the thermal interfacial reaction was previously proposed [1]. The process enables remarkably low leak current of the film due to the lack of carbon impurity. We applied N_2 plasma for the interfacial reaction and nitridation and realized plasma-based nanoparticle involved non-thermal chemistry for HfSiON.

2. Experiment

The system consists of a UHV-SPM chamber with an e-beam metal evaporation source, a separate VHF (50MHz) low pressure ICP plasma source [2], and ex-situ XPS. Commercial Si(100) wafer with native oxide is introduced to the chamber and Hf and Ti metal beam is exposed to the surface at room temperature. The morphological development of the surface is analyzed with the in-situ non-contact AFM. The N_2 ICP is exposed to the sample without any temperature control. The grown film surface is again evaluated on its surface flatness with nc-AFM. The change of the chemistry of the sample surface is analyzed with the XPS.

3. Results and discussion

The AFM image of self-assembled Hf nanoparticles on SiO_2 surface after the deposition reveals dome shaped particles with 3-6 nm width are close-packed on the surface with high density of 8.5×10^{12} cm^{-2}. The N_2 ICP exposure induces the interfacial reaction of the Hf nanoparticle/SiO_2/Si structure and forms Hf(Ti)SiON(film)/SiON/Si. The angle-resolved Si*2p* XPS spectrum at 101.5 eV in 30deg. shows the Si included in the film is nitrided. Hf silicate formation is found in the component around 100 eV. The total amount of nitrogen atoms in the film well corresponds to the total supply from the N_2 ICP due to the absorption spectroscopy of $N(^4S)$ and $N(^2D)$ [2].

The AFM image shows the film has superior flatness of RMS roughness of 0.3 nm except the dips of 0.8 nm depth which disappear with Ti addition to the film.

5. Conclusions

The novel film growth process with plasma induced reaction of metal nanoparticles and the substrate is demonstrated for Hf(Ti)SiON. The process scheme is widely applicable to the nano-scale feature modification and chemistry with non-thermal reactions of non-equilibrium plasma.

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9:40am **PS+TF-ThM6 Platinum and Platinum Oxide Films Prepared by Using Low Temperature Plasma Enhanced ALD**, ***B.H. Liu**, C.C. Kei, C.C. Yu, D.R. Liu, C.N. Hsiao*, National Applied Research Laboratories, Taiwan, Republic of China

In this study, smooth and pinhole-free platinum films were deposited on Si substrates by plasma enhanced atomic layer deposition (PEALD). Ar/O_2 inductively coupled plasma was applied to decompose the ligands of Pt precursor, $MeCpPtMe_3$. Partial pressures of Ar and O_2 were held at 0.3 and 0.1 Torr during the PEALD process, respectively. The substrate temperatures were varied between 100 and 200 ^oC to obtain Pt films. Crystal structure of deposited films was studied using an X-ray diffraction (XRD). Film morphology was obtained by using a field-emission scanning electron microscope (SEM). Electric properties of deposited films were measured by using a Hall effect measurement system. XRD pattern shows that the film prepared at 200 ^oC has the fcc structure of platinum. Only a broad (102) peak of hexagonal alpha-PtO_2 was appeared for the films deposited at 100 and 150 ^oC, implying that oxidized Pt can not be reduced at a temperature less than 200 ^oC. The growth rate of Pt films is about 0.04 nm/cycle based on the SEM observation. The sheet resistances of Pt and PtO_2 film prepared by using 200 cycles are 30.57 and 85.19 o hm/ sqr, respectively.

Keywords: inductively coupled plasma, PEALD, sheet resistance

10:40am **PS+TF-ThM9 Dielectric Performance of Al_2O_3 Films Prepared by Direct Plasma PEALD**, ***C.C. Yu**,* Instrument Technology Research Center, Taiwan, Republic of China*, Z.Y. Han,* National Chiao Tung University, Taiwan, Republic of China*, C.C. Kei, M.Y. Tsai, W.H. Cho, C.N. Hsiao,* Instrument Technology Research Center, Taiwan, Republic of China*, C.H. Chien,* National Chiao Tung University, Taiwan, Republic of China*, C.Y. Su, N.N. Chu*, Instrument Technology Research Center, Taiwan, Republic of China

In this study, plasma enhanced atomic layer deposition system (PEALD) was used to deposit Al_2O_3 films at room temperature. Trimethylaluminum (TMAl) and O_2 plasma were used as metal precursor and oxidant, respectively. A DC power supplier was applied to generate O_2 plasma with a parallel-plate electrode configuration. Nitrogen purge was applied between the exposures of TMA and O_2 plasma to prevent vapor phase reaction. Cycle numbers of PEALD were varied from100 to 500 nm. The thicknesses of Al_2O_3 films were obtained from x-ray reflectivity measurement. Surface morphology and roughness was given by using scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. C-V measurement was performed by using a HP4194 impedance analyzer to obtain the capacitance and dielectric constants. I-V curves were characterized by measuring with a Keithley 4832 multimeter. The growth rate of Al_2O_3 film increases with the increasing plasma power and reaches a saturation value of 1.7 Å/cycle when the plasma power exceeds 50 W. SEM images imply PEALD prepared Al O films have a pin-hole free structure, and AFM result shows that Al_2O_3 film deposited for 100 PEALD cycles has a smooth surface roughness as 0.211 nm. The dielectric constant for Al_2O_3 films prepared by using 100 PEALD cycles is 4.53. A leakage current density of 3×10^{-9} A /cm^2 can be achieved for the 100 PEALD cycles prepared Al_2O_3 film. The interface charge trap density given by the C-V measurement increases with an increasing plasma power. This implies that high energy oxygen ion bombardment would lead to damage at interface and formation of the charge traps.

Key : PEALD, Parallel-plate electrode, Direct plasma, High-k material, C-V, I-V, D_{it}

11:00am **PS+TF-ThM10 Improving the Quality of PVD Cu Seed Layer for Interconnect Metallization**, *A. Dulkin, E. Ko, L. Wu, I. Karim, K. Leeser, K.J. Park,* Novellus Systems, Inc.*, **L. Meng**, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Physical Vapor Deposition (PVD) of Ta(N) barrier and Cu seed layers has been traditionally used in interconnect metallization process flow in VLSI manufacturing. Reliability of the manufactured devices greatly depends on the quality of different interfaces, particularly the barrier/seed one. Failure to ensure continuous seed coverage with good adhesion to the barrier may result in voided electrofill, post-CMP defects, and stress/electro-migration failures. Quality of the barrier/seed interface was greatly improved by enhancing Cu nucleation on the Ta surface through filtering of non-energetic species from the deposition flux, increasing the fraction of Cu ions, improving flux uniformity, and minimizing gas ion bombardment. The self-sputtering ability of Cu was combined with magnetically confined high density plasma in the Novellus HCM^{TM} PVD source. Spatial profiles of plasma density and temperature, as well as ion flux, ion metal fraction, and ion energy, were measured by planar Langmuir probes, quartz crystal microbalance, and gridded energy analyzer, all located at the wafer level. Multiple criteria, such as seed step coverage and roughness, its resistance to agglomeration, and its stability in the plating bath, have been used to evaluate interface quality. As a result new and improved Cu PVD process which demonstrated superior stability during subsequent process steps and ensured successful electrofill performance with more than 50% reduction in minimal sidewall thickness requirement has been developed.

11:20am **PS+TF-ThM11 Pulsed Plasma Polymerization of 2-Chloro-p-xylene**, ***I.C. Estrada-Raygoza**, P.L.S. Thamban, G. Padron-Wells, L.J. Overzet, M.J. Goeckner*, University of Texas at Dallas

11:40am **PS+TF-ThM12 Morphological Variation of Plasma Polymerized TiO_xC_y Films as a Function of Oxygen Concentration during PECVD**, ***L. Sun**, H. Jiang,* General Dynamics Information Technology*, J. Grant,* University of Dayton Research Institute*, P. Lloyd,* UES, Inc.*, T. Bunning, R. Jakubiak*, Air Force Research Laboratory

Amorphous titanium oxide derivative films have relatively high index of refraction compared to purely organic thin films, retain much of the functionality of their crystalline counterparts and can be deposited at low temperature. Using PECVD operated at room temperature and in a remote configuration, plasma-polymerized (PP-) $TiO_xC_yN_z$ films were derived from titanium (IV) isopropoxide using a mixture of argon and nitrogen as carrier gases. Upon exposure to ambient, the PP-$TiO_xC_yN_z$ films undergo a continual decrease in film thickness and increased index of refraction that does not stabilize for several days after deposition. After one hour in air, the thickness of the films rapidly decreased by 14% and after three weeks the thickness decreased 30% (128 - 90 nm). This was accompanied by an increase of the refractive index from n_{589} = 1.72 to 1.84. Broadly, the densification results from oxidation of low valence titanium moieties prevalent in films formed in an oxygen-poor environment. From AFM and SEM studies we know that the thin films possess a featureless, smooth (RMS - 0.5 nm) one phase 3-D crosslinking amorphous structure. When oxygen was substituted for nitrogen as a carrier gas, most of the titanium atoms retained the Ti^{4+} state of the monomer and little, if any densification was noted; however, the film morphology was strongly dependent on the argon to oxygen ratio in the carrier gas mixture. In oxygen rich conditions, the films contained granular columns (approximately 10 to 50 nm in diameter) composed of amorphous TiO_2, with void and crack defects between 10-20 nm in width. Films deposited in oxygen poor conditions exhibited a uniform, amorphous structure as seen in the nitrogen/argon case.

Plasma Science and Technology
Room: Aztec - Session PS-ThM

Plasma Surface Interactions (Fundamentals & Applications) III
Moderator: S. Sriraman, Lam Research Corporation

8:20am **PS-ThM2 Etching of MTJ by using Non-Corrosive Gas Mixtures**, ***S.K. Kang**, M.H. Jeon, J.Y. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Magnetic random access memory (MRAM) has made a prominent progress in memory performance and has brought a bright prospect for the next generation nonvolatile memory technologies due to its excellent advantages. Dry etching process of magnetic thin film is one of the important issues for the magnetic devices such as magnetic tunneling junctions (MTJs) based MRAM. MTJs which are the basic elements of MRAM can be used as bits for information storage. CoFeB is a well-known soft ferromagnetic material, of particular interest for magnetic tunnel junctions (MTJs) and other devices based on tunneling magneto-resistance (TMR), such as spin-transfer-torque MRAM. One particular example is the CoFeB–MgO–CoFeB system, which has already been integrated in MRAM. In all of these applications, understanding and control over the etching properties of CoFeB is crucial. Recently, transferring the pattern by using an Ar^+ ion milling is a commonly used, although the redeposition of sputter etch products on the sidewalls and the low etch rate are main disadvantages of this method. Other method, which reported the etch rates higher than 50 Å/s

for magnetic multilayer structures using Cl_2/Ar plasmas, is also proposed. However, the chlorinated etch residues on the sidewalls of the etched features tend to severely corrode the magnetic material. To prevent corrosion of MTJ layer, the etching of MTJ layer using organic-based gases such as CO/NH_3, CH_3OH, etc. are actively investigated currently.

In this work, MTJ materials such as CoFeB, MgO, etc. were etched using various gas mixtures which can be expected to form volatile metallo-organic compounds and the results were compared with those etched using Cl_2-based gas mixture. As one of the gas mixtures, gas mixtures of carbon monoxide (CO) and ammonia (NH_3) were used as etching gases to form carbonyl volatiles, and the etched features of CoFeB thin films under by Ta cap-material were observed with transmission electron microscopy. The etch results showed the enhanced etch rates higher than 3 times by using a gas mixture of CO/NH_3 compared to that etched by pure CO or NH_3 possibly indicating the formation of products composed of carbonyl volatiles. The composition of etched sidewall was less damaged compared with that etched with Cl_2-based gas. The characteristics of etched MTJs were also compared to the MTJs etched by the other method such as neutral beam etching, etc.

8:40am **PS-ThM3 Effect of SiH_4 Addition on the Sidewall Passivation Mechanism during the Anisotropic Etching of III-V Materials in Cl_2-based ICP Discharges**, ***L. Gatilova***, *S. Bouchoule, G. Patriarche, S. Guilet*, Cnrs - Lpn, France

III-V semiconductors remain unequalled materials to fabricate high efficient emitters. Anisotropic etching of III-V heterostructures is a key building-block for the processing of such photonic devices (e.g. low-optical loss waveguides or optical cavities with high quality factors, ...) and the ICP etching technique is now widely used for this purpose. Several Cl_2-containing chemistries have been proposed to date for the smooth and high-aspect-ratio etching of InP-based or GaAs-based heterostructures required to reach the NIR region. We have evidenced that in many cases anisotropic etching is due to a passivation mechanism involving SiOx deposition on the III-V sidewalls [JVSTB 26, 666 (2008)]. SiOx passivation simply occurs when a Si wafer is used as the sample tray; this configuration corresponds actually to most commercial ICP etch systems having an electrode diameter of 4-in or more, used to etch III-V samples of not more than 2-in size. However this will not be the case in future large surface processing of III-Vs, when the III-V wafer becomes of the same size of the electrode, or when III-V dies bonded onto a 200/300mm wafer have to be etched, with the wafer surface covered by protecting layer that is not silicon as it may be the case in III-V/Si photonic technologies. Other passivation mechanisms have therefore to be found. For example a Si-containing gas could be added in order to maintain SiOx passivation. In this work we have investigated the Cl_2-SiH_4 chemistry for this purpose. It is found that highly anisotropic etching (aspect ratio > 30 for micropillars) of III-V patterns with a high etch rate (> 0.6 µm/min) can be obtained by optimizing the SiH_4/Cl_2 ratio, independently from the nature of the sample tray. A high selectivity > 1:30 is also obtained with the process using a metallic/ dielectric mask. Ex-situ EDX-TEM analysis of the thin (10-50 nm thick for a 3-µm etch depth) passivation layer deposited on the sidewalls of etched sub-micrometer pillars shows that in optimized conditions this layer consists of micro-crystalline silicon We also confirm that the deposition of the passivation layer is enhanced by H addition, as previously proposed in Cl_2-H_2 chemistry [JVSTA 27, 262, 2009]. We will further discuss the possibility to use HBr/SiH_4 plasma for the anisotropic etching of InP-based or GaAs-based heterostructures, and the effect of oxygen or nitrogen addition in the gas phase on the composition of the passivation layer. We also will compare the respective effects of $SiCl_4$ and SiH_4 addition on the etched surface passivation process.

9:00am **PS-ThM4 Deep Inductively Coupled Plasma Etching of GaN**, ***J. Ladroue****, GREMI - STMicroelectronics, France, *M. Boufnichel*, STMicroelectronics, France, *T. Tillocher, P. Lefaucheux, P. Ranson, R. Dussart*, GREMI, France

III-Nitride semiconductors such as gallium nitride are widely used in light emitter device manufacturing[1]. GaN physical properties also open new prospects in microelectronics developments[2]. Combining a wide bandgap (3.4eV), strong chemical bonds and high electron mobility, GaN based devices should operate under higher temperature, higher power and higher frequency than typical silicon devices. Due to inert chemical nature of GaN, wet etching is limited[3]. As a consequence, it is necessary to use dry etching method[4] to obtain a reliable MESA structure. Chlorine based plasmas are commonly used because $GaCl_3$ is the most volatile etching product. Etch rate is also found to strongly depend on physical sputtering. GaN etching requirements for power device applications are different from those concerning photonic devices. Due to the power density supplied to the next generation of power devices, deep structures as high as 10µm should be build. As a comparison, the etched depth needed for light emitter are of the order of a few hundreds of nanometers. Deep GaN etching implies etch rate issues as well as surface roughness defects. We showed that these etching defects are linked with dislocations and nanopipes inherent to the substrates and revealed during etching[5]. Experiments were mainly performed in two Inductively Coupled Plasma (ICP) reactors: an industrial Alcatel 601E, composed of an ICP source and a diffusion chamber and an ICP-RIE Corial 200IL without diffusion chamber. For a better understanding of the etching mechanisms, different diagnostics are used to characterize the plasma. Optical emission spectroscopy, Langmuir probe and mass spectrometry are performed as a function of process parameters. We observe that etching behaviour depends on cover plate material. An optimum etch rate as a function of source power is measured by using a silicon cover plate. OES and Langmuir probe measurements suggest that silicon cover plate, which is etched by chlorine radicals, can be a limitation in the etching performance of the process. Different chemistries are studied as source of active species, sputtering ions or molecule scavenging impurities. We have shown that oxygen impurities are responsible for the columnar defects. We also show that adding a small amount of nitrogen in the chemistry could increase the selectivity with SiO_2 mask.

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9:20am **PS-ThM5 Mass-selected Ion Beam Study on Reactive Ion Etching Mechanisms for Pt, Co and PtCo Thin Films**, ***K. Karahashi***, *T. Ito, S. Hamaguchi*, Osaka University, Japan

Recently limited choices of microfabrication techniques for magnetic thin film processing have been recognized as one of the major impediments for the development of microelectronics devices such as magnetic random access memory (MRAM) and read/write heads for magnetic data storage. For magnetic films, Ar ion milling is essentially the only etching technique that is currently available in actual manufacturing processes. Whereas Ar ion milling is a well established technology, it does not provide etching selectivity that the industry currently desires. For magnetic thin films, reactive ion etching processes based on Cl2 or CO chemistry have been considered so far as good candidates. In this study, therefore, we have examined etching processes of PtCo alloy thin films by energetic Cl+ ions. More specifically we have measured desorbed products and etching yields of Pt, Co, and PtCo, using a mass-selected ion beam system. With the use of the ion beam system, we inject mono-energetic single-species ions (i.e., Cl+ or Ar+ ions) to the sample surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with a quadrupole mass spectrometer (QMS), a temperature programmed desorption (TPD) system, and an X-ray photoelectron spectroscopy (XPS). It has been found that the etching yields of Pt films by Cl+ ion injections are larger than those of Co films by Ar+ ion injections, and the etching yields of PtCo depend on its composition ratio. It has been also found that platinum chloride (PtClx) desorption are detected with QMS under Cl+ ion injections. These results indicate that the yield of Pt is increased by the formation of PtClx on the surface. We have also studies temperature dependence of the etching yield. With a higher temperature, the yield of Pt by Cl+ ion injections is lower because chlorine coverage on the surface is also lower at a higher surface temperature. Therefore temperature control in Pt or PtCo etching processes is of significant importance for better process control. Etching characteristics of PtCo by CO+ ion beams will be also discussed.

9:40am **PS-ThM6 Oxygen and Chlorine Atom Recombination on TiO_2, SiO_2, and SiO_xCl_y-Coated Plasma Chamber Wall Surfaces**, ***R. Khare***, *V.M. Donnelly*, University of Houston

Recombination and other possible reactions of Cl and O on chamber walls in chlorine and oxygen plasmas were studied by the “spinning wall” technique. With this method, a small cylinder (1”dia. x 1”high) in the chamber wall was rapidly rotated, periodically exposing its surface to the plasma and then to the differentially pumped diagnostic chamber housing an Auger electron spectrometer for *in-situ* surface analysis. The plasma chamber also contained a silicon electrode that can be rf-biased and sputtered in an inert (Ar) plasma, or etched in a chlorine plasma. Using this technique, we previously measured Cl and O atom recombination on plasma-conditioned anodized Al and stainless steel surfaces by monitoring desorption of Cl_2 and O_2 with a mass spectrometer or through a pressure rise. We also previously found a substantial increase in O atom recombination probabilities due to trace amounts of Cu deposited *in-situ* by thermal evaporation. In the current study, a smooth Ni-coated Al substrate

* Coburn & Winters Student Award Finalist

was used. This substrate was exposed to Si sputtered from the rf-biased electrode and was then oxidized and conditioned by long exposure to oxygen plasma. Traces of Ti were deposited on this surface with the evaporator, followed by the oxygen plasma conditioning (Ti:Si:O::5:47:48 atomic percents, averaged over the ~10 nm depth probed by Auger). The O atom recombination probability on this Ti-contaminated substrate was found to be ~30% lower than on the Ti-free substrate, i.e. the opposite to that observed for Cu contamination. Ti was then etched away in the chlorine plasma, leaving an oxy-silicon-chloride surface (Si:O:Cl:: 47:39:14). The Si electrode was then etched in the chlorine plasma while rotating the substrate, coated the rotating substrate with etching products changing the substrate surface composition to Si:O:Cl :: 54:19:27. Immediately after extinguishing the rf bias to the Si electrode, the Cl atom recombination probability was found to be lower than on the more oxygen-rich Si surface. During rf bias, however, the total product yield is higher, indicating that other products (i.e. $SiCl_x$) could also be desorbing from the substrate as a result of the etching of the Si electrode.

10:40am **PS-ThM9 Characteristics of Silicon Nitride Etching by Reactive Plasmas Containing CHxFy Ions**, ***T. Ito***, *K. Karahashi,* Osaka University, Japan, *M. Fukasawa, T. Tatsumi,* Sony, Japan, *S. Hamaguchi*, Osaka University, Japan

Selective etching of silicon oxide (SiO2) over silicon nitride (SiN) has been widely used in microelectronics fabrication processes such as contact hole etching in self-aligned processes, formation of a stress liner, and dual/triple hard mask (DHM/THM) etching processes of dual-damascene structures. The etching gases used in these plasma processes typically include fluorocarbon gases and etching chemistry by CxHyFz+ ions emitted from the plasma is considered to play an important role for the determination of etching selectivity. In this work, etching characteristics of SiO2 and SiN by CHxFy+ ion beams are discussed with a special emphasis on effects of hydrogen provided by CHxFy+ ions on etching selectivity. The ion beams are generated by a mass-selected ion beam system and injected with a monochromatic energy into a sample substrate (SiO2 or SiN) placed in an ultra-high vacuum chamber. The multi-beam injection system that we employed for this study also allows simultaneous irradiation of the sample by charge-neutral radical species during ion beam injection. In this way, the system enables us to simulate experimentally plasma-surface interactions that take place during the corresponding plasma etching processes. The change in chemical nature of the substrate surface during the process can be observed *in situ* by X-ray photoelectron spectroscopy (XPS) that is installed in the reaction chamber. Time of Flight (ToF) measurement of sputtered species from the sample surface is also possible with a mass and energy analyzer placed near the sample. In the experiments, sputtering yields of SiO2 and SiN by CF+,CHF+, CF2+, CF2+, and CH2F2+ ion beams generated from CH2F2 or CHF3 gases were examined. A typical ion dose for each ion irradiation was $1.6´10^{15}$ /cm^2/sec. It has been found that the sputtering yield of SiN depends on the amount of hydrogen provided by the CHxFy+ ion beam whereas the sputtering yield of SiO2 is less sensitive to such hydrogen. Energy dependence of the sputtering yields and effects of fluorocarbon film deposition by a low-energy ion beam on hydrogen accumulation on the surface will be also discussed.

11:00am **PS-ThM10 H_2/Ar and D_2/Ar Plasma Interactions with a-C:H Surfaces: A Detailed Study of Modified Layer Formation and Erosion**, ***N. Fox-Lyon***, *F. Weilnboeck, G.S. Oehrlein,* University of Maryland, *N. Ning, D.B. Graves*, University of California at Berkeley

The interaction of H_2 gas discharges with carbon-based materials has been of sustained interest in many technological fields. In this work we have used a well characterized, inductively coupled plasma system (ICP) to study the interaction of H_2/Ar and D_2/Ar discharges with hard a-C:H films. The erosion of a-C:H is monitored in real time by ellipsometry, optical emission spectroscopy and plasma properties are characterized by a Langmuir probe. Our experimental setup allows for varying the reactor geometry over a wide range by changing the plasma generation substrate distance. H_2/Ar and D_2/Ar plasma interaction with a-C:H were performed using low pressure (30 mTorr) 600 W 13.56 MHz RF inductive power plasma with different substrate bias voltages. Employing real-time ellipsometry, we were able to monitor the detailed kinetics of the formation of a 1-5 nm thick hydrogenated layer of lower density than the a-C:H substrate, followed by steady-state erosion. The influence of various plasma parameters on modified surface properties and erosion will be reported. We also will present real-time data which gives insight into the dynamic flux of carbon atoms into the plasma produced by erosion a-C:H for different conditions . The measurements of the modified surface layers are compared with “Stopping and Range of Ions in Matter (SRIM)” simulations for different conditions. The atomistic details of surface processes will also be be compared with molecular dynamics simulations of the UCB group.

We gratefully acknowledge support of this work by DOE’s *Plasma Science Center for Predictive Control of Plasma Kinetics: Multi-phase and Bounded Systems (University of Michigan).*

11:20am **PS-ThM11 Plasma Surface Interactions for Low-*k* Material Etching**, ***M. Hori***, Nagoya University, Japan **INVITED**

Porous low-dielectric-constant (low-*k*) materials such as porous SiOCH film are essential for interlayer dielectric film in high performance ULSI devices. To establish extremely precise etching processes of the low-*k* film for the next generation devices, it is required to understand the surface reaction and damage formation mechanism during plasma processing, while developing a sophisticated methodology to control the etching and ashing processes. We developed an integrated monitoring system equipped with in-situ spectroscopic ellipsometry, Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS), a substrate temperature monitor using an optical fiber-type low-coherence interferometer [1] and an absolute density monitor for H and N radicals [2,3]. The integrated monitoring system was installed in a dual frequency capacitively coupled plasma etch reactor and we investigated H_2/N_2 plasma interactions on the low-*k* film. The in-situ monitoring during the plasma etching or ashing is crucial for the clarification of damage mechanism because the damaged films are easily modified during air exposure. Furthermore, the effect of each particle, i.e. ions, photons and radicals, was investigated individually by ‘PAPE’ method [4] that uses small plates, such as Si, SiO_2 and MgF_2, on or above the film substrate during the plasma exposures. So far, we considered that damages on the p-SiOCH are determined by chemical reactions of H radicals that reduce the Si-CH_3 bonds and N radicals that have an effect of inhibition of the damages. It was also confirmed that a portion of Si-O-Si linear structure in the SiOCH film changed to network and cage structures with decrease in Si-CH_3 bond during the plasma exposure. The effects of the temperature during etching on the etch profile were also examined for a variety of H_2/N_2 gas mixture ratio. The higher the H radical density and the temperature, the lager the undercut in the low-*k* pattern profile. Especially, the temperature increase after plasma ignition was found to be a cause of the profile deformation. Based on the above results, we proposed an autonomously-controlled etch system that realized a real-time feedback control for the fine pattern etching while monitoring the wafer temperature, radical densities and so on. It was demonstrated that real-time radical-density control upon the temperature was effective for obtaining precise pattern profiles.

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Plasma Science and Technology
Room: Aztec - Session PS1-ThA

Plasma Modeling
Moderator: Z. Chen, Applied Materials Inc.

2:00pm **PS1-ThA1 Molecular Dynamics Simulation of Fluorocarbon/hydrogen Ion Beam Interaction with a PMMA (Polymethyl Methacrylate) Surface**, ***Y. Morita**, M. Isobe, S. Hamaguchi*, Osaka University, Japan

Beam-surface interaction between fluorocarbon ions (mainly CF3+) or hydrogen ions (H+) with a polymethyl methacrylate (PMMA) surface has been examined at the atomic level with the use of molecular dynamics (MD) numerical simulations. The work is motivated by the desire to control line edge roughness (LER) or line width roughness (LWR) observed after plasma etching processes, which is incurred by deterioration of photoresist polymers exposed to reactive plasmas. Molecular structures of commercially available photoresist polymers are complex in general and typically not disclosed in the public domain, so we use PMMA in this work as a model polymer in a hope that, combining this study with other previous studies on plasma-polymer interaction based on other simple organic polymers, an insight into the mechanism of photoresist deterioration due to plasma exposure will be gained. For example, PMMA contains ester bonds (R-COO-R') and their interactions with plasmas are a subject of this study. In this presentation, we shall focus on two specific issues. One is to evaluate sputtering yields of PMMA by Ar+ or CF3+ ion injections with various injection energies. With Ar+ injection simulations, we shall clarify the nature of physical sputtering of PMMA whereas, with CF3+ injection simulations, we hope to understand the modification mechanism of a polymer mask during oxide etching processes. Our MD simulation results have so far indicated that there is a strong dependence of sputtering yields on the direction of polymer chains against the incoming beam angle at the atomic level. The other issue is solidification of polymer by hydrogen plasma exposure, which may be used to cure polymers after the mask formation process by photolithography. In the simulations, hydrogen beams are injected into PMMA and we have observed increase of the relative carbon density in the polymer due to hydrogen abstraction reactions.

2:20pm **PS1-ThA2 Molecular Cross-Section Calculations Enabling Etch-Profile Simulations of a Microwave Source Silicon Etch using Ar/HBr/O_2**, ***J. Munro**, J. Tennyson,* University College London, UK*, S.-Y. Kang,* Tokyo Electron Limited, Japan*, D. Brown*, Quantemol Ltd., UK

The introduction of new microwave plasma sources for Silicon and Silicon-Nitride etch processes has renewed interest in a more detailed understanding of the etch process in a microwave regime. The use of Ar/HBr/O_2 for Silicon etching in this regime is common. In particular the inclusion of HBr has been found to reduce "microtrenching" [1]. The etching yields of high density HBr plasmas have been studied previously [2]. Here we study the additional effects of the etching products SiBr and $SiBr_2$ near the wafer.

A set of quantum electron scattering calculations are performed on SiBr and $SiBr_2$ using the electron-molecule code Quantemol-N [3]. The resulting cross-sections are used to complete a set of gas-phase reactions contributing to the etch process. Etch-profile simulations are then performed using the Monte Carlo Feature Profile Model code (MCFPM) [4]. Here we use incident species fluxes derived from simulations of Ar/HBr/O_2 plasmas. Results are presented which include an analysis of the contribution of the etch products SiBr and $SiBr_2$.

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2:40pm **PS1-ThA3 Gas/Ion Temperatures in Multi-Frequency Capacitively Coupled Plasma Sources**, ***A. Agarwal**, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma etching of high aspect ratio (HAR) features is extremely challenging as it places great emphasis on uniformity of just about every characteristic of the plasma: density, fluxes, fields, energy and angular distributions to mention a few. At large aspect ratios, even minor variations in the bulk plasma can translate into huge deviations on the feature scale. One important plasma characteristic that influences etch properties is the ion temperature. Small variations in ion temperature can lead to non-uniform or tapered etch profiles since even marginally cold ions when accelerated through the sheath (having large voltage drops for HAR process) can deviate significantly from the normal leading to offset of the bottom of the feature compared to the top.

In this work, a 2/3 dimensional plasma equipment model (CRTRS) [1] has been used to assess the consequences of ion and neutral temperature on etching processes. CRTRS previously only included continuity and momentum equations for charged species. The model has been improved to include solution of the energy equations for all heavy neutral and charged species to obtain the ion and neutral temperatures. The model results have been validated using experimental data from laser induced fluorescence measurements.[2] In this talk, results of this validation exercise will be discussed. We found that while ion temperatures peak in the sheath region near the electrodes under the influence of high electric fields, neutral radicals' temperature peak predominantly in the bulk via collisions with ions (for example, charge exchange reactions). Consequently, inclusion of Franck-Condon heating sources is important for low fragmenting gas mixtures such as pure Ar compared to, for example, N_2 to accurately predict neutral temperatures.

The validated model is then applied to a typical high-power HAR etch process. Modeling results are used to understand the impact of gas and ion temperatures on electron heating and power deposition mechanisms, ion energy and angular distributions, plasma uniformity and neutral radical composition. Plasma characteristics are investigated for etch-relevant feed gas mixtures over a wide range of pressures (20 – 100 mT).

[1] A. Agarwal, P.J. Stout, S. Rauf and K. Collins, 56th AVS Symposium 2009.

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3:00pm **PS1-ThA4 Control of Electron Energy Distributions in Pulsed Capacitively Coupled Plasmas Sustained in Noble and Electronegative Gas Mixtures**, ***S.-H. Song**, M.J. Kushner*, University of Michigan, Ann Arbor

In capacitively coupled radio frequency (rf) discharges, as used in plasma processing of semiconductor materials, controlling the electron energy distribution function $f(\varepsilon)$ is important for controlling the flux of radicals and ions to the substrate. The strategies for controlling $f(\varepsilon)$ include varying the gas mixture, frequency, pressure and pulse power format. Customizing the $f(\varepsilon)$ is related to balancing the electron heating and cooling mechanisms. Multi-frequency capacitively coupled plasmas (CCPs) provide an opportunity to customize $f(\varepsilon)$ through using pulsed plasmas. For example, a low frequency (LF) is typically applied to the lower electrode to control ion energy distributions and a high frequency (HF) is applied to the upper electrode to heat electrons. By pulsing the HF one can modulate $f(\varepsilon)$ to produce shapes that are not otherwise attainable using continuous wave excitation. For example, an $f(\varepsilon)$ may be produced that has both a high energy tail and a large thermal component. These $f(\varepsilon)$ will produce different dissociation patterns in the feedstock gases. The choice of pressure, duty cycle and pulse repetition frequency (PRF) are important to the time average $f(\varepsilon)$ as these determine the relative role of thermalization. Pressure also has a role in determining the dominant electron heating mechanism between ohmic heating and stochastic heating.

The customization of $f(\varepsilon)$ in 2-frequency CCPs will be discussed using results from a 2-dimensional plasma equipment model. The electron $f(\varepsilon)$ are obtained using a Monte Carlo simulation including electron-electron collisions. The consequences of PRF, duty cycle and HF power on $f(\varepsilon)$ will be discussed for pressures of tens of mTorr in argon and fluorocarbon gas mixtures. The correlation between these parameters and $f(\varepsilon)$ on the identity of radical and ion fluxes onto the substrate will be made.

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

3:40pm **PS1-ThA6 Impact of Frequency Mixing on Plasma Characteristics in Low Pressure Capacitively Coupled Discharges**, ***J.A. Kenney**, S. Rauf, K. Collins*, Applied Materials Inc.

As high aspect ratio (HAR) etch requirements have grown more stringent, the strategies used to deliver an appropriate combination of species to the wafer have evolved considerably. One common approach is to use a capacitively coupled plasma (CCP) reactor with a combination of generator frequencies and complex feed gas mixtures. The use of multiple frequencies allows for generation of a large plasma density using a high frequency

source while biasing the wafer substrate at low frequency to control the flux and energy of impinging ions. Complex feed gases provide etch precursors from which to make volatile products as well as passivating species to protect certain features (e.g. sidewalls). Such a large parameter space of frequencies, powers, pressures, and feed gases to employ, however, has made modeling an increasingly attractive option to gain insight and understanding, both during engineering design and process development. Here, we use a plasma model to investigate the impact of frequency mixture in low pressure capacitively coupled discharges.

In our 2/3-dimensional fluid plasma model, charged species densities are computed by solving continuity equations for all species coupled with the full momentum equation (ions) or the drift-diffusion approximation (electrons). These equations, combined with the Poisson equation, which governs the electrostatic fields, are solved implicitly in time. The electron temperature is determined by solving the electron energy equation. The model also includes the full set of Maxwell equations in their potential formulation, Kirchhoff equations for the external circuit, and continuity equations for neutral species, along with non-uniform mesh generation to better resolve regions of interest. Ion energy and angular distributions are computed using a Monte Carlo-based particle simulation, which uses the spatially and temporally-resolved species densities, species fluxes, and electric fields from the plasma model as inputs.

In this work, we look at the impact of multiple frequencies on plasma density, uniformity, fluxes of neutrals and ions, and ion energy distributions. We consider frequencies in the range of 1 to 150 MHz in single-, dual-, and three-frequency configurations in CCP systems using a simple etch-relevant feed gas mixture (Ar/CF_4) at 20 mT. Radio-frequency (RF) bias powers in the 1.0 – 7.0 kW range are employed.

4:00pm **PS1-ThA7 Predicting the Surface Response Upon Simultaneous Plasma Etching and Deposition**, ***N.P. Marchack**, C. Pham, J. Hoang, J.P. Chang*, University of California Los Angeles

As the downscaling of integrated circuit devices continues, minute variations in the feature profiles from processing techniques such as plasma etching significantly affect device performance . Thus, there is a need to predict the surface response during etching of a variety of materials, such as complex oxides. To accurately represent the kinetics involved, experiments are conducted in this work in an inductively coupled plasma (ICP) reactor equipped with a quadrupole mass spectrometer (QMS) for analyzing etch products and a quartz crystal microbalance (QCM) for measuring the etch rate *in situ*. This reactor is connected to a UHV transfer tube which allows the surface composition to be studied via x-ray photoelectron spectroscopy (XPS) without exposure to ambient conditions. The materials system studied include Hf-based high-k materials and $YMnO_3$, a multiferroic oxide, etched in Cl_2/BCl_3 plasmas. A surface site-based phenomenological model[1] that was previously developed for binary and ternary oxides is shown to be applicable to the prediction of how these complex oxides were etched. To use this model in a cell based Monte Carlo simulator to predict feature profile evolution, a translated mixed layer (TML) kinetics model[2] is utilized to describe the surface reactions such as ion impingement, neutral adsorption, physical sputtering and chemically enhanced ion etching. Reaction parameters that cannot be measured directly are extracted by comparing the model to etch yield data and validated against the phenomenological model. Ion incident angle dependence and an elliptical energy deposition model were used to capture the effects of surface morphology on the profile evolution under the bombardment of energetic and directional ions. Simulated profiles are compared to cross-sectional SEM images of the patterned material systems and display reasonable agreement.

[1] Martin et al. Journal of Vacuum Science and Technology A 27(2) 2009

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4:20pm **PS1-ThA8 Computational Modeling of DC and Pulsed Microplasmas-Based Space Propulsion Devices**, ***L. Raja***, The University of Texas at Austin **INVITED**

Very small microplasma-based propulsion is gaining importance as a viable propulsion concept for small satellites that weigh less than 100 kg. These devices involve complex multiple physical phenomena associated with high-density plasma discharge in small volumes and coupling of plasma phenomena with high-speed viscous dominated flows. Specific requirements of minimal wall erosion and wall heat transfer are also driving oscillatory dielectric-barrier microdischarge designs, which introduced additional physics complexity associated pulsed microplasmas. We present computational modeling studies of microplasma propulsion devices. The model describes the plasma dynamics, gas-phase chemical kinetics, neutral dynamics, and coupling of plasma phenomena with high-speed flow for both DC and pulsed mode microdischarges. Unique computational challenges associated with this problem are described and solutions to these challenges as addressed in our model are presented. Results show the dominant mechanism for thruster performance improvement is the gas heating in the microplasma. The gas heating is primarily a result of near-wall ion Joule heating in the case of DC discharges and is also accompanied by significant wall heat loss. The use of dielectric-barrier microdischarge configuration accompanied by oscillatory excitation is shown to mitigate wall heat loss while sustaining off-wall gas heating.

5:00pm **PS1-ThA10 Feature Profile Simulator FPS-3D**, ***P.E. Moroz***, TEL US Holdings

Reliable and predictive feature profile evolution simulation is an extremely important topic for nanotechnology and semiconductor industry. If successfully solved, it will allow significant saving of time and resources presently spent on numerous design experiments directed on finding proper chemistries and conditions in a multi-parameter space of search for advanced etching or deposition. FPS-3D is a Monte Carlo code, where launched particles corresponding to the specified fluxes, each particle typically consisting of many gas molecules, or ions, or electrons, interacts with solid materials of the target. A cellular model is used for presenting solid materials. Each cell is a complex object consisting of the body of the cell and its surface layer, and is typically includes many molecules. All material properties and all reaction mechanisms are specified in the chemistry file. The output of gas and ion reactions is characterized in terms of probabilities and yields. The incoming fluxes could be specified via two different options. One option is to use the flux file, where all the data for fluxes of each gaseous species is provided for each energy-angular bin. This file is typically generated by a plasma simulation code (for example, such as HPEM [1], which we are currently using). A second option is to generate fluxes of species according to a few parameters specified in the input file. The second option is especially convenient for considering interactions of particle beams with solid materials. Upon collision of a flux particle with the target, the code determines a particular cell where the reaction occurs. The result of such an interaction could be a removal of some of molecules from the cell, or deposition of similar or different molecules to the cell, or both. The code considers low-energy gaseous species very differently from the high-energy species. The low-energy species are interacting only with the surface layer of the cell by mainly depositing or altering molecules in the surface layer, although spontaneous etching from the surface layer is taken into account as well. The energetic species, on the other hand, could do much more. They could also lead to removal of molecules from the surface layer and from the body of the cell with the yield corresponding to their energy and angle of incidence. Such yields could be larger than one for higher energies. This report will present technical details of FPS-3D and give a few examples of its operation in 2D and 3D. The author is thankful to Drs. S.-Y. Kang of TEL TDC and P. Miller of HFS for valuable discussions.

[1] M.J. Grapperhaus, M.J. Kushner, J. Appl. Phys. 81, 669 (1997).

5:20pm **PS1-ThA11 3D Numerical Modelling of VHF MHC type SiH_4 PECVD for Solar Cells**, ***J. Joo***, Kunsan National University, Republic of Korea

Full 3D numerical modelling is done for a VHF (very high frequency > 30 MHz) MHC (multi hollow cathode) based PECVD (plasma enhanced chemical vapor deposition) of Si thin film in tandem or triple junction solar cells. The purpose of VHF-MHC is confining high density plasma into small holes while maintaining large area deposition uniformity. ICP gives high plasma density (> 10E11 #/cm3) but poor uniformity and thin film quality (electron mobility and photo sensitivity) in addition to particle generation issues. For optimization of hole geometry and hole array configurations, numerical models for Ar, H2, and SiH4 are developed based on fluid model. CFD-ACE+ is used for calculation of each parameter set. For Ar, 1 Torr and 40 MHz was good enough for confining into a few mm diameter holes, but H2 needs higher plasma density. SiH_4 needs more complicated plasma chemistry sets including negative ions and higher order silanes. The concentration ratio of SiH3/SiH2 was accurately modeled using electron energy distribution function calculation.

Plasma Science and Technology
Room: Galisteo - Session PS2+BI-ThA

Plasmas for Medical and Biological Applications
Moderator: S. Hamaguchi, Osaka University, Japan

2:00pm **PS2+BI-ThA1 Activation of Cell under the Atmospheric Pressure Plasma Irradiation**, ***T. Hirata**, C. Tsutsui, A. Mori, T. Yamamoto, A. Taguchi*, Tokyo City University, Japan **INVITED**

The researches in the case of "novel plasma" have been widely conducted in the fields of chemistry, solid physics, and nanomaterial science. Such

plasma uses a boundary reaction field in a liquid or gaseous-liquid phase based on application of liquid plasma, micro plasma, and atmospheric pressure plasma. In particular, atmospheric pressure plasma is indispensable not only for sterilization, disinfection, decomposition of hazardous materials, and surface modification but also for the cultivation and development of complex new areas which require a diverse perspective, involving biomedical science. From the above-mentioned background, we are conducting basic experiments on direct irradiation of cells using a micro-spot atmospheric pressure plasma source.

The device is a coaxial structure having a tungsten wire (1 mm I.D.) installed inside a glass capillary (plasma generation area: 8 mm I.D.; tip area: 1 mm I.D.), and a grounded tubular electrode wrapped on the outside. The high voltage for the plasma generation is provided by the high voltage power supply. The conditions of plasma generation are as follows: applied voltage: 5-9 kV, frequency: 1-3 kHz, helium (He) gas flow rate: 1 L/min, and plasma irradiation time: 1-300 sec. The experiment was conducted by preparing a culture medium containing mouse fibroblasts (NIH3T3) on a culture dish (made of polypropylene). A culture dish irradiated with plasma was introduced into a CO_2-incubator.

According to the dependency of cell numbers against the plasma irradiation time, when only He gas was flowed, the growth of cells was inhibited as the floatation of cells caused by gas agitation inside the culture was promoted. On the other hand, there was no floatation of cells and healthy growth was observed when plasma was generated. Therefore, it appears that the interaction due to ion/radical collisions on the culture surface causes a substantial effect on the proliferation of growth factors such as epidermal growth factor (EGF), nerve growth factor (NGF), and transforming growth factor (TGF) that are present in the cells.

2:40pm **PS2+BI-ThA3 Stability of Highly Functionalised Plasma Polymerised Acrylic Acid Thin Films in Aqueous Environments**,
C.D. Easton, *A. Pegalajar Jurado, A. Badri, S.L. McArthur*, Swinburne University of Technology, Australia

Plasma polymerisation provides a convenient one step method for creating a functionalised organic surface on virtually any substrate. This technique has attracted considerable attention in recent years for application within the biomedical field as a substrate for cell culture and as a surface functionalisation for polymer grafting and protein immobilisation *[1-4]*. Detailed stability studies of these coatings in aqueous solutions have focused on water rather than more biological relevant solutions including phosphate buffered saline (PBS). Critically, the interplay between coating stability and protein and polymer adsorption on the coating behaviours have rarely been examined.

Within this study, highly functionalised acrylic acid thin films have been fabricated via RF plasma polymerisation and the stability of these coatings in aqueous environments examined. The chemical and physical stability of these coatings in water and PBS were investigated using X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and Quartz Crystal Microbalance with Dissipation (QCM-D). The results have shown that the physical behaviour of the coatings changes significantly when they are exposed to water and buffers with differing pH and ionic strength. The significance of these stability observations in an application setting has been explored where the plasma polymerised acrylic acid coating has been used in the assembly of polyelectrolyte layers and biomolecule immobilisation.

References:

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3:00pm **PS2+BI-ThA4 Scalable Atmospheric DBD Device for Biomedical Processing**,
S. Kitazaki, *T. Iwao, G. Uchida, K. Koga, M. Shiratani,* Kyushu University, Japan, *N. Hayashi*, Saga University, Japan

Nonthermal atmospheric discharge plasmas have been employed for biomedical processing applications, because they offer low temperature processing [1-3]. We have developed a scalable atmospheric dielectric barrier discharge (DBD) device for biomedical processing in a large area. The device consists of 12 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. In principle, the device size can be extended to a large area by increasing the electrode length as well as the number of electrodes. The electrodes are arranged parallel with each other at a distance of 0.5 mm. The frequency of applied voltage was 10 kHz, and its peak-to-peak voltage was 10 kV. The peak discharge current was about 0.15 A and the duration of each current pulse was about 10 ns. To obtain information about radicals generated in the discharges, UV-Visible emission spectra were measured with a multi-channel spectrometer. Spectral lines of N_2 2nd positive band (280-400 nm) were observed in air DBD discharges. We apply the device to process seeds of radish sprouts. We compare germination and growth of seeds with one minute plasma irradiation to those of seeds without irradiation. While the germination periods of these two kinds of seeds are 2 days, being nearly the same with each other, the growth rate of irradiated seeds is 20-50% faster than that without irradiation. These results suggest that the DBD device is useful for such biomedical processing applications.

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3:40pm **PS2+BI-ThA6 2010 AVS Medard Welch Award Lecture - Controlling Plasma Sources: Nano to Bio**,
N.Yu. Babaeva, S.-H. Song, University of Michigan, Ann Arbor, *J. Shoeb, M. Wang,* Iowa State University, *Y. Yang,* Applied Materials, Inc., ***M.J. Kushner****, University of Michigan, Ann Arbor **INVITED**

The development of technologies for plasma modification of surfaces is in large part based on controlling plasma sources to deliver desired fluxes of radicals and ions to surfaces. Doing so ultimately rests on the ability to control the energy and velocity distributions of charged and neutral particles. Controlling electron energy distributions, *f(e)*, ultimately specifies the production rates of radicals and ions. Controlling the velocity distributions, *f(**v**)*, of ions and neutrals ultimately specifies the activation energy delivered to surfaces. There has been an evolution of techniques to control *f(e)* and *f(**v**)* utilizing type of excitation (e.g., ICP vs CCP), frequency, pulse power and, most recently, multiphase plasmas These techniques are being challenged to provide the specificity required for nano-scale processing, particularly given the synergistic and presently uncontrolled relationship between fluxes into and returning from surfaces. Control of *f(e)* and *f(**v**)* becomes even more challenging in biological applications of plasmas and plasma medicine, typically performed at atmospheric pressure, where timescales for plasma formation are shorter than conventional control techniques can address. In this talk, techniques to control *f(e)* and *f(**v**)* in plasma sources in the context of plasma modification of biological and nano-scale surfaces will be discussed. Examples of control techniques will be taken from using pulsed, multi-frequency and multi-phase plasmas. Applications will be discussed from nano-scale cleaning and sealing of porous dielectrics; and dielectric barrier discharge treatment of wounded skin. Challenges facing researchers in developing plasma sources having the ability to control *f(e)* and *f(**v**)* will be discussed.

* Work supported by the Department of Energy Office of Fusion Energy Sciences, Semiconductor Research Corp., Applied Materials, Tokyo Electron., Agilent, Inc.

4:20pm **PS2+BI-ThA8 Spectral Signatures of Amine Species at Aminated Surfaces Prepared by using Plasma Techniques, Self Assembling of Thiols and Silanization**,
W.E.S. Unger, *N. Graf, P.M. Dietrich, H. Min, P.-L. Girard-Lauriault, A. Lippitz, T. Gross*, BAM Federal Institute for Materials Research and Testing, Germany

The determination of amines on surfaces capable of binding biomolecules is important for the understanding and optimization of technologically relevant coupling processes. Different relevant types of amino-functionalized model surfaces have been investigated by complementary tools of surface analysis: XPS, NEXAFS spectroscopy and ToF-SIMS with Principal Component Analysis. Amino-terminated surfaces have been prepared from aliphatic and aromatic aminosilanes and aminothiols by self assembly, plasma polymerization of allyl amine and plasma activated polyethylene foils reacted with 1,2-diaminoethane. The determination of those amino groups which are available to serve as attachment sites for biomolecules in technical applications by wet chemical derivatization (CD) XPS using 3,5-bis(trifluoromethyl)phenyl isothiocyanate was a special issue of interest. In another experiment the in-depth homogeneity of a pulse plasma polymerized allyl amine film after derivatization with 4-trifluoromethyl benzaldehyde (TFBA) was investigated by using variable excitation energy XPS. Finally, effects of aging in air and damage by X ray radiation on aminated surfaces are addressed.

Problems of the CD XPS approach for a determination of amines will be discussed with a focus of comparability of results obtained in different labs.

* Medard W. Welch Award Winner

4:40pm **PS2+BI-ThA9 Correlation of Properties of Polymeric Organic Layers with Plasma Parameters***, S. Umrath, F. Schamberger,* ***G. Franz***, Hochschule Muenchen, Germany

For exact deposition of thin films out of the vaporous phase (cvd), an entire knowledge of the process parameters such as flows, pressure and gaseous temperature is required. In the case of pecvd, this means the extension on influencing plasma variables like plasma density and electron temperature, in particular in large reactors for production purposes to meet the demands for flat layer qualities (growth and composition) over the whole reactor volume.

In an almost cubical reactor 80 l in volume, the microwave power is coupled into the volume via a quartz window which exhibits approximately 1/10 of the sidewall area. The spatial compilation of these plasma quantities along with plasma potential has been accomplished with a bendable Langmuir probe. To isolate the tungsten wire against its grounded housing tube, it was coated with polyparylene. After having compared this construction with our Langmuir probe which has been now in use for more than a decade, we have taken data of the whole reactor with argon and with mixtures of monomers of parylene and argon or oxygen in a pressure range between 10 mTorr and 150 mTorr (1 1/2 Pa to 20 Pa) applying a new evaluation procedure [1]. Over the covered range, the plasma density remains in the dielectric regime (plasma degree less than 100 ppm).

Compared to discharges through pure argon, the plasma parameters exhibit opposing behavior: at same discharge pressure and power input, the plasma density is lower, whereas the electron temperature goes up. The layers are highly transparent with a slightly yellow color. Ftir measurements reveal that the ring structure still remains intact. Adding oxygen to the ambient to the monomeric vapor leads to hydrophilic surfaces which is caused by the formation of CO bonds and OH bonds. The creation of these features is confined by power input. If it is raised beyond 4 W/l, the reaction mechanism drastically changes from surface polymerization to volume polymerization leading to thick, low-density films which can be easily be scratched away. This change has been traced by plasma diagnostics and mass spectrometry. At a threshold density of about 1 x 10^{10}cm^{3} (plasma degree about 1000 ppm), all peaks beyond 44 (CO_2) vanish. In the resulting mass spectrum, no CH vibrations beyond 3000 cm^{-1} can be detected indicating the complete destruction of the aromatic system.

[1] Peter Scheubert: Modelling and Diagnostics of Low Pressure Plasma Discharges, PhD thesis, Bochum, 2002

Plasma Science and Technology
Room: Southwest Exhibit Hall - Session PS-ThP

Plasma Science and Technology Poster Session

PS-ThP1 Transition in Intensities of the Forbidden Atomic Oxygen Spectral Lines and its Application to Plasma Monitoring, ***V. Milosavljevic,*** Dublin City University, Ireland & University of Belgrade, Serbia*, A. Jasenko,* Faculty of Pharmacy, Serbia*, Z. Simic, L.C. Popovic*, Astronomical Observatory, Serbia

To decouple the optical contributions of surfaces in a process chamber to the plasma chemistry from those of other constituents present in the plasma is one of the most demanding tasks today. In this work oxygen spectral emission is used for purposes to increase understanding of plasmas such as those used in industry and particularly those used in semiconductor device manufacture, when plasma-surface interactions are of critical importance.

We analyze the intensity of forbidden oxygen lines at 630.0, 636.3, 297.23 and 557.73 nm as well as the (NLTE afflicted) oxygen triplet lines around 777.4 nm. The emission of forbidden spectral lines is used to establish a threshold for actinometry. Actinometry suffers from signal masking by molecular species due to molecular dissociation and trace gas emission. To establish the threshold for actinometry we monitor the emission of forbidden spectral lines and search for “phase transition” in the intensities of forbidden spectral lines (in most cases the upper energy levels of atomic forbidden lines are below the threshold for dissociation of any constituent molecule so that any sudden increase in the emission intensity of forbidden lines indicates molecular dissociation has occurred). Concurrently the forbidden spectral line is used for determination of the main plasma parameters too.

Radiative emission of the forbidden spectral lines follows a three level atomic model that characterize the radiative transfer processes, and can help to understand the contribution of molecular dissociation processes to the emission spectrum of atomic oxygen. This represents a major contribution to the current state of the art and eliminates the requirement for trace gas based actinometry which will overcome not only the molecular masking problem but the intrinsic problem of having a trace gas in the plasma discharge. Thus, this work develops the method based on OES as a non invasive technique for quantifying complex chemistry which has direct application in plasma processing in semiconductor and other industries. This approach enables greater understanding of complex processes allowing, optimization, fault detection, increased productivity and yields. The challenge in this case lies in the complex plasma chemistry that is commonly used in surface treatment and the constraint of applying intrusive sensors to industrial plasma reactors. These constraints make OES ideal for industrial use, however interpreting the spectra and extracting useful information is the challenge. This work is done with ICP 13.56 MHz RF plasma discharge at pure oxygen, as well at oxygen-argon-hydrogen mixture.

PS-ThP2 Optical Emission and Mass Spectrometric Characterization of a Dual Plasma PE-CVD System, ***Z. Chen****, V.M. Donnelly, D.J. Economou*, University of Houston

Initial diagnostic studies will be presented of a novel PE-CVD reactor suitable for self-limiting growth of thin films through a repetitive, step A / step B, process. In a single vacuum system, two independent plasma sources are operated to separate step A from step B. An Ar gas curtain minimizes mixing of the gases of the two plasma sources. As an example, this reactor could be used to deposit a very thin hydrogenated amorphous silicon (a-Si:H) film in step A, followed by exposure of this film to a hydrogen plasma in step B, to induce formation of silicon nano-crystallites. In the present reactor configuration, one plasma source is a capacitively-coupled plasma (CCP) reactor and the other is an inductively-coupled plasma (ICP) reactor. The substrate is moved back and forth between the two sources. Optical emission spectroscopy (OES) and mass spectrometry (MS) are used to detect radicals (OES) and stable feed gas and products (MS) in the two plasma sources. Results will be presented for a SiH_4/He CCP and H_2, N_2 or O_2 ICPs operating simultaneously. The degree of separation of the two plasma sources will be presented as a function of the Ar flow rate to the gas curtain, as well as the feed gas flow rates and pressures of the plasma sources.

PS-ThP3 Diagnosis of Gold Nanoparticle Synthesis in Solution Plasma by Coherent Anti-Stokes Raman Spectroscopy*,* ***D. Fujimoto****, J. Hieda, M.A. Bratescu, O. Takai, N. Saito*, Nagoya University, Japan

The performance of the electrical discharges in the aqueous solution presents modern and ecologically very attractive way of the synthesis of nanoparticles. Such kind of techniques are known for the production of very active species like hydrogen radicals, hydroxyl radicals, ozone, aqueous electrons, UV light, etc., which are characterized by its very high reactivity. Although both oxidation and reduction agents were generated in the plasma, gold, platinum, and copper ions were reduced by the plasma. In order to control the reactions in solution plasma, the understandings of activated species and their behaviour are needed.

In this paper we present process diagnosis of gold nanoparticles synthesis in solution plasma based on coherent anti-stokes Raman spectroscopy (CARS). This discharge is generated between two wire type electrodes faced one to each other and driven by bipolar dc pulse power supply. Utilization of this power supply gave us a possibility of an intensive and stable working condition even at lower liquid conductivities. Operation conditions of this power supply lie in the frequency range 0-50 kHz, with minimum pulse length, 2 ms, and maximum voltage, 1.5 kV. In order to obtain desired conductivity of liquid, a small amount of KCl was added into the water. Initial $[AuCl_4]^-$ concentration and pH were varied. The reactor was placed on the stage of the optical microscope with CARS system. The morphology of the nanoparticles obtained was observed by transmission electron microscopy (TEM). The solution after discharge was also analyzed by UV-Vis spectroscopy and ICP-MS.

PS-ThP4 Characterization of a Faraday-shielded Inductively Coupled Plasma using Langmuir Probe and Optical Emission Spectroscopy, ***W. Zhu****, H. Shin, L. Xu, V.M. Donnelly, D.J. Economou*, University of Houston

A novel plasma reactor was designed and built to control the electron energy distribution function (EEDF) in the plasma, as well as the ion energy distribution (IED) and ion angular distribution (IAD) on the substrate electrode. The main inductively coupled plasma (ICP) source has a Faraday shield to minimize the RF component of the plasma potential. The substrate electrode and another electrode in contact with the plasma (boundary electrode) can be biased independently with DC or RF voltages to influence the IED and IAD. A second tandem ICP plasma source may be used to inject a secondary plasma or metastable atoms to the main source, to influence the EEDF. A continuous wave argon plasma in the main ICP was characterized with a Langmuir probe (LP), with and without the Faraday shield installed. With the Faraday shield, the DC value of the plasma potential decreased from 25 to 17 V, and the corresponding peak-to-peak amplitude of the RF oscillation dropped from ~15-20 V to ~0.8-1.5 V, compared to the case without the Faraday shield. A low plasma potential is critical for certain processes such as atomic layer etching with monolayer precision. The electron “temperature” as well as the ion and electron densities were measured for a range of powers and pressures. The plasma density was $1.5\times10^{-12}cm^{-3}$ at 40 mtorr and 300 W. The EEPF was also measured with the LP; comparisons with EEPFs extracted using trace rare gas-optical emission spectroscopy (TRG-OES) will be presented. In addition to argon, oxygen and krypton plasmas were studied and their similarities and differences with the argon plasma will be shown. Control of the plasma potential and hence energy of ions impacting surfaces was achieved by applying a positive DC voltage to a boundary electrode immersed in the plasma. Finally, preliminary results of plasma injection from the secondary to the main plasma source and its effect on the EEDF will be presented.

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PS-ThP5 Diagnostic of Laser Ablation Air Plasma using Wide Field Spectroscopy, *N. Abundiz,* UNAM-CICESE, Mexico, *C. Velez,* UABC, Mexico, *E. Luna, S. Zazueta,* Universidad Nacional Autónoma de México*,* ***R. Machorro***, Universidad Nacional Autonoma de Mexico

PS-ThP6 ***In-situ*** **Monitoring of Organic Pollutants Degradation in Pulsed Plasma by Coherent Anti-Stokes Raman Spectroscopy***,* ***M.A. Bratescu****, N. Saito, O. Takai*, Nagoya University, Japan

Water pollution and storage is becoming an important problem to the people worldwide. Conventional water treatment processes, such as chlorination and ozone oxidation suffer a lot of limitations. The application of pulsed electrical discharges in water solutions for degradation of organic pollutants offers the advantage of simultaneous using of different physical effects (UV light) and chemical effects by the active species like OH, H, O, HO_2, H_2O_2,

O_3 able to decompose the harmful organic compounds. In this study we analyzed the degradation of the benzoquinone molecule by using *in-situ* Coherent anti-Stokes Raman Spectroscopy (CARS) in order to monitor the active species during the decomposition process.

In the present experiment a pulsed plasma in an aqueous benzoquinone solution was used. The plasma was generated in a reaction glass cell, between two rods electrodes. The plasma electrical characteristics were: the peak to peak voltage of 2 – 4 kV, the pulse frequency of 10 – 15 kHz and the pulse width of 2 µs. The reaction cell was set on the optical microscope stage of the CARS system. Benzoquinone was dissolved in a potassium sulfate solution (4 g/L) and the pH was adjusted with dilute sodium hydroxylate or dilute sulfuric acid.

The CARS benzoquinone signal was observed at 1230 cm^{-1}, 1050 cm^{-1} and 1667 cm^{-1} corresponding to COH bending CH, bending and CC stretching vibrations, respectively. Degradation of the benzoquinone molecule was monitored by the peak at 1667 cm^{-1}, characteristics to benzene ring vibration. The shift and the amplitude of the absorption peak at 427 nm were observed by *ex-situ* measurements by the UV-visible spectroscopy.

The degradation of benzoquinone molecule depends on solution pH and plasma electrical characteristics.

PS-ThP7 Study of Plasma-based Ion Implantation Sterilization using High Resolution Rutherford Back Scattering, ***T. Tanaka***, *T. Hironaka,* Hiroshima Institute of Technology, Japan*, S. Hayashi,* Japan Medical Creative, Japan*, I. Koyama*, Saitama Medical University, Japan

Plasma base ion implantation (PBII) with negative voltage pulses to the test specimen has been applied to the sterilization process as a technique suitable for three-dimensional work pieces. Pulsed high negative voltage (5µs pulse width, 300 pulses/s, -800 V to -13 kV) was applied to the electrode in this process at a gas pressure of 2.4 Pa of N_2. We found that the PBII process reduced the numbers of active Bacillus pumilus cell using N_2 gas self-ignitted plasma generated by only pulsed voltages. The number of bacteria survivors was reduced by 10^{-5} x with 5 min exposure. As the ion energy is the most important processing parameter, a simple method to estimate the nitrogen ion energy calculated using distribution for nitrogen in Si implanted by PBII was estimated. The ion implanted surface using PBII sterilization is discussed from measurements data using the High Resolution Rutherford Back Scattering (HR-RBS) .

PS-ThP8 A Novel Current-Voltage Probe for Diagnostics in Deposition Plasma, ***M.B. Hopkins***, *D.M. O'Sullivan*, Impedans Ltd., Ireland

Current- voltage probes monitor power parameters, such as the voltage, current and phase angle of an RF power used to generate the plasma (source) or to bias a substrate. A number of commercial systems are available and a key feature is that the sensors work in non-50Ω environment. This allows the sensor be placed either pre-match or post-match and still make accurate measurements.

The most important plasma parameters in a capacitively coupled plasma source or bias configurations are the flux and energy of ions arriving at the substrate. The ion flux is difficult to establish in deposition tools as the plasma often deposits insulating layers, such as in the manufacture of solar panels.

We report on a novel IV sensor, which is placed post-match in series with a capacitively coupled RF biased plasma electrode. The sensor integrates the current into voltage bins. We show that the resulting characteristic represents the real current-voltage (IV) characteristic of the electrode. The measured IV trace is similar to a DC Langmuir probe IV trace and we determine the ion flux to the biased electrode. We compare ion flux measured by the IV probe with the ion flux determined by a retarding field analyzer placed on the electrode.

Other parameters such as electron temperature and plasma potential are also obtained and compared to direct measurements taken in the source.

PS-ThP9 Hardness and Roughness of SiCN Thin Films Deposited at 500 °C by RF-PECVD, *T. Wydeven,* ***T. Kawabe***, SAMCO International, Inc.

The experimental difficulties encountered in attempting to synthesize super hard high purity polycrystalline or single crystal beta carbon nitride (β-C3N4) films has prompted research on the synthesis of hard silicon carbon nitride (SiCN) films(1). Current research interest in SiCN is motivated by several reported desirable properties of this material(2). Among those properties are short bond length, high bond strength and therefore high hardness, adjustable friction coefficient, high resistance to wear and corrosion and wide band gap.

The work reported on here is a continuation of our earlier research (3) on the deposition and characterization of near stoichiometric SiCN films deposited at ambient temperature from a gas mixture (SiH4, CH4, N2) and using RF-PECVD. In this work, we report on the hardness and characterization of surface topography by roughness measurements and SEM photographs of SiCN films deposited at 500 °C on silicon wafer substrates using RF-PECVD. These measurements are important in applications involving friction, lubrication and wear(4).

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PS-ThP10 The Role of Negative Oxygen Ions in the Pulsed-Plasma Deposition of Titania Films, ***J.W. Bradley***, *R. Dodd, S.D. You*, University of Liverpool, UK

Reactive pulsed magnetron sputtering is the process of choice to deposit commercially important oxide-based thin films and coatings. The technique relies on the plasma ions (e.g. Ar^+, O^+) assisting the deposition process through energetic impact at the substrate leading to good, dense coating structures.

However, in these systems copious amounts of negative ions (O^-, O_2^- O_3^-, MO_x^-) can be created at the cathode target. These ions are accelerated through the cathode sheath to bombard the substrate with upper energies equivalent to the target potential, (i.e. hundreds of eV). These ions easily overcome the negative substrate bias potentials, used to attract positive ions and can be wholly destructive to growth of engineering quality films.

In this study we use an eclipse laser photo-detachment technique combined with a Langmuir probe to measure the density of negative ions in the pulsed sputtering of titanium in oxygen-argon mixtures. This has been done at different positions in the plasma during different phases of the driving pulsed-voltage waveform. The results show that the total negative ion density can exceed that of the electrons and at positions close to the substrate on the discharge centre line, the fraction of very fast negative ions can be over 10% of the total observed. The power fluxes of these species at the substrate have been calculated and the effect on the growing TiO_2 film is discussed.

PS-ThP11 Investigation of the Plasma Parameters and Plasma Process-Induced Damage in Physical Vapor Deposition, ***X. Tang***, *T.-J. Gung, S. Gandikota, P. Gopalraja, R. Wang, G. Liu*, Applied Materials Inc.

The introduce of the high K and metal gate enables significant gate leakage reduction (>100x) with excellent transistor performance. Physical vapor deposition process plays an important role in its manufacturing process because of its film composition tunability, excellent step coverage and thin film uniformity. However there are growing concerns about the potential process damage induced by the physical vapor deposition process since in some cases these films are directly deposited on thin (~20A) high k films. It is well known that PID can be classified into three categories: charging damage by plasma non-uniformity, bombardment damage by high energy ions, neutrals, and electrons, and radiation damage from plasma emission.In this paper, we mainly focus on high energy components in plasma itself and the process induced damage caused by the plasma non-uniformity. Both the discharge plasma properties (such as ne , Te, target voltage , ion energy etc) and their correlations to the potential plasma process induced damage were discussed. Two types of PVD chamber designs were evaluated in this study. One is a short throw rf PVD chamber which has both RF and DC power capability on the sputtering target. Another one is a long throw dc sputtering chamber with a special high ionization magnetron. Ti target material is used in this study. Discharge plasma parameters such as (plasma density ne, electron temperature Te, and plasma potentials Vpl) were monitored by a Langmuir probe inserted into the discharge cavity. The corresponding neutral and ion energy were further derived based on the measured target voltage and wafer self-induced dc bias. The plasma uniformity is characterized by an ion current probe biased at the ion saturation region. Two test vehicles: the 'Spiders ' wafer with different ANT ratios and MOS cap were used to quantify the plasma process induced damage.

Langmuir probe studies show that the rf plasma density increases linearly with the rf power while

the electron temperature remains constant in RF PVD chamber. Very high metal ionization was achieved as a result of the high plasma density by high rf power and high pressure (>50mT)operation. Interestingly, no plasma process induced damage were observed by RF PVD Chamber under a broad range of process conditions even with different ion energy.On the other

hand, with the dc high ionization (magnetron with a UB>3.5) operation,significant plasma damage was observed under most conditions. The damage was later correlated to the plasma non-uniformity.These results clearly demonstrates that plasma non-uniformity needs to be optimized

for any PVD hardware for the damage sensitive applications.

PS-ThP12 Realization of Silicon Antireflection Subwavelength Structure using Simple One Step Plasma Fabrication Process, ***B.S. Kim***, *J.H. Sung, M.W. Lee, C.H. Choi, H.D. Yim, S.G. Park, S.G. Lee, E.H. Lee, B.H. O*, INHA University, Republic of Korea

Polished flat silicon surfaces have high reflectivity in visible lays. The minimization of reflection losses is very important for solar cells. Lowering surface reflectivity of silicon by texturization is one of the most important processes for improving the conversion photovoltaic efficiency of silicon solar cells.

Many texturing techniques for fabricating antireflective silicon surfaces have been proposed, including mechanical diamond saw cutting, optical interference lithography, wet etching using catalysis of metal, and reactive ion etching, to produce so-called “black silicon”.

In this paper, we attempted to one step etching for formation of black silicon using combinded Cl_2, C_4F_8, and O_2 gases. It uses inductively coupled plasma (ICP) and Cl_2 gas for etching, C_4F_8 and O_2 gas for masking.

The substrate temperature was -10 °C ~ 10 °C, the fluorocarbon film deposited in a C_4F_8 plasma was thicker and more strongly bonded than the lower substrate temperature. Then combinded O_2 gas, fluorocarbon film was locally etching which is self-masking effect. The diameter of fluorocarbon mask was dozens nanometer size.

With Cl_2 etching, many processes were developed for producing vertical sidewalls, smooth surface morphology, fine critical dimension control, and high aspect ratio microstructures for MEMS. The main advantage of Cl_2 etching is that etching is anisotropic since it is an ion assisted process rather than a spontaneous etching process. The subwavelength silicon pillar structure was grown up because physical etching characteristic of Cl_2 plasma.

The etched silicon surface shows almost zero reflectance in the visible region. The silicon surface is covered by columnar microstructures. The diameter and height of subwavelength silicon columnar structures were depends on substrate temperature, etching, and gas contain ratio.

PS-ThP13 Synthesis of Zinc Oxide Nanoparticles Using an Atmospheric Pressure Plasma Jet, ***S.M. Chang***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Nanocrystalline zinc oxide particles have been synthesized using a gas-phase process by atmospheric pressure plasma jets (APPJ). The APPJ used is sustained by a repetitive pulse source with nitrogen or oxygen as the plasma gas. Zinc-containing salt solutions, namely $Zn(NO_3)_2$ and $ZnCl_2$, are nebulized into μm-sized droplets and fed into the downstream of the APPJ. Liquid droplets undergo vaporization and reaction and form solid particles in the downstream of the jet. The particles are collected using de-ionized water or buffer solutions. The particle size and its distribution are measured using the dynamic light scattering method and scanning electron microscopy. It is found that the reactivity and the temperature of the jet downstream are able to efficiently convert the droplets into crystalline ZnO particles, as confirmed by the X-ray diffractometer. When O_2 is used as the plasma gas, the fabricated ZnO particles readily dissolve in the particle-collecting solution due to the decrease in the pH of this solution. The pH drops to as low as 1 within 2 min. It suggests the need of using the buffer solution as the particle collector. When using N_2 as the plasma gas, a relative small change in pH is found and results in decent collection yield. When using $Zn(NO_3)_2$ solution as the precursor under 275 V applied voltage and 30 ~ 60 slm N_2 gas flow, the fabricated ZnO particles show a double-peak distribution: small and large particles with the averaged sizes of 120 nm and 1000 nm, respectively. Preliminary studies found that the particle size distribution can be altered by changing the precursor solution concentration, the carrier gas flow rate, and the plasma conditions. Finally, the potential using this apparatus to fabricate more complex metal oxides will be discussed.

PS-ThP14 Studies of Interactions between the Plasma in Salt Solutions and Organic Compounds, ***S.H. Wang***, *H.W. Chang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Plasmas in salt solution have shown to be reactive due to the produce of reactive species such as OH, H, O, and H_2O_2. In this study, interactions between the plasma in salt solutions and organic compounds are studied. The plasma is ignited in sodium-, zinc-, or calcium-containing salt solutions using DC or AC power sources. The electrode at which the plasma is ignited is a platinum wire 0.5 mm in diameter covered by a glass tube while the grounding electrode is a bare platinum wire of the same diameter. Cellulose, glucose and lactose are used as the organic compounds studied. Diagnostics include a voltage probe and a current probe to monitor the electrical characteristics; the conductivity and pH of the solution before and after the plasma treatment are monitored; an optical emission spectrometer is used to monitor the time-averaged emission spectra. It is observed that with the existence of the cellulose particles in the solution, the plasma appears to be much less stable. In addition, a much stronger light emission and larger current fluctuations are seen. This is possibly due to the fact that stable bubble is not able to form due to the existence of the cellulose particles. When glucose or lactose are added in NaCl solution, a much brighter plasma is seen and the optical emission shows a hump-like continuous emission band between 400~800 nm while this emission band does not exist without the addition of glucose and lactose. The total organic carbon (TOC) and high performance liquid chromatography (HPLC) measurements strongly suggest the possibilities that the cellulose, glucose, and lactose are decomposed due to the interaction with the plasma ignited in salt solution, especially when the plasma electrode is negatively biased. The identification of the decomposed products is currently underway. In this presentation, how the existence of the organic compounds influences the plasma behavior and how the organic compounds are decomposed in the plasma will be discussed.

PS-ThP15 The Optical Diagnostics of Microplasmas in Different Types of Electrolyte Solutions, ***A.H. Hsieh***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

The optical diagnostics of microplasmas in various electrolyte solutions are performed. This microplasma is sustained by using a DC power source with the voltage up to 600 V. The powered electrode, the electrode where the plasma is ignited, consists of a thin platinum wire 0.5 mm in diameter covered by a glass tube. The grounding electrode is a bare platinum wire of the same diameter. Both electrodes are immersed in the solution. The electrolyte solutions studied include NaCl, $NaNO_3$, Na_2SO_4, $ZnCl_2$, $Zn(NO_3)_2$ and $ZnSO_4$ with the concentration of 0.01 M ~ 2 M . Time-averaged optical emission and time-resolved intensities of the light emanating from the plasma are studied. With an applied voltage greater than 500V and the concentration below 0.02 M, there exists a bubble that stays steadily at the electrode tip for many seconds, and microplasma is ignited inside the bubble. Under this condition, the emission of H, OH, O and atomic metal emissions are observed regardless of the electrolyte type. In the high concentration conditions and low applied voltages, atomic metal emissions dominate and nearly no H, OH, and O emissions are seen. It is observed that for all electrolyte solutions studied except NaCl, there exist a hump-like continuous emission band in the optical emission spectra between 400~900 nm. The source of this continuous band is not identified yet but can potentially be a result of the thermal emission or free-bound transition. In this presentation, the implication of the optical emission to the plasma reactivity will be discussed.

PS-ThP16 Polyimide Surface Treatment by Using Atmospheric Pressure Plasma to Improve Metal Adhesion, ***J.B. Park***, *J.S. Oh, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Polyimide [(N, N′-oxydiphenylene) pyromellitimide], (PI) is one of the representative high-performance polymer films that has been widely used for the substrate in the microelectronic and flexible electronics industries because PI has desirable properties of high temperature resistance, good mechanical strength, and good dimensional stability. However, in spite of the extensive usage as well as the detailed characterization of the PIs, the poor adhesion of metals to PI, which is a consequence of its low specific surface energy, has to be overcome to render the fabricated devices reliable because the general polyimide–metal composites have limited adhesion strength. Therefore, many researchers have studied on the surface modification of PIs for adhesion improvement to metals.

In this study, the surface of PDMA-ODA PI films before and after atmospheric pressure plasma surface treatment by using remote type modified DBD module was investigated to improve the adhesion between the PI substrate and metal thin film using various gas compositions such as $N_2/He/SF_6$, $N_2/He/O_2$, N2/He/SF_6/O_2, $N_2/He/SF_6/O_2$. Among the plasma treatments of the PI substrate surface using various gas mixtures, the plasma treatment with $N_2/He/SF_6/O_2$ showed the lowest contact angle value due to the high C=O bondings formed on the PI surface while that with $N_2/He/SF_6$ showed the highest contact angle value due to the high C-F_x chemical bondings on the PI surface. Especially, when O_2 gas was varied from 0 to 2.0 slm in N_2(40 slm)/He(1 slm)/SF_6(1.2 slm)/O_2 (x slm) gas composition, the lowest contact angle value of about 9.3° could be obtained at 0.9 slm of O_2 gas due to the highest oxygen radicals in the plasma, which forms the highest C=O bondings on the PI surface. When the interfacial adhesion strength between the Ag film and the PI substrate was measured after the treatment with N_2(40 slm)/ He(1 slm)/SF_6(1.2 slm)/O_2(0.9 slm) followed by the deposition of Ag, the peel strength of 111 gf/mm which is close to the

adhesion strength between metal and the PI treated by a low pressure plasma could be observed.

PS-ThP17 Atmospheric Pressure Plasma Ashing of Photoresist using Remote-type Pin-To-Plate Dielectric Barrier Discharge, ***J.S. Oh**, J.B. Park, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

In these days, many researchers are developing glow discharges generated at atmospheric pressure for various thin films and surface processing such as dielectric barrier discharge (DBD), microwave discharge, pulsed corona plasma, etc. Various atmospheric pressure plasma sources have been reported with the claim of low running cost, low gas temperature, and wide applicability to surface treatment, cleaning, etching, and thin film deposition. Among the various atmospheric pressure plasmas, DBDs are studied mostly due to the easy generation of stable plasma.

In this study, ashing of photoresist (PR), AZ 1512, has been investigated using a pin-to-plate remote type DBD. The pin-to-plate type DBD showed higher power consumption and higher discharge current compared to the conventional DBDs at a given applied voltage. But glow discharge, which is generated by DBD, is easily transferred to filamentary/arc discharge, and the substrate is more likely to be damaged under arc discharge condition. Also, thermal damage can occur due to direct contact of the plasma to the substrate. But, remote plasma does not contact the substrate directly, therefore, the substrate can avoid damaging. In this study, using the remote type pin-to-plate DBD, the effect of various gas combinations such as N_2/O_2, N_2/O_2+SF_6 on the changes of PR etch rate and the electrical characteristics was investigated.

The addition of SF_6 gas to N_2/O_2 showed higher consumed power, higher discharge current at a given voltage, and lower turn-on voltage. For example, the plasma turn-on voltage for N_2 (50 slm)/O_2 (200 sccm) was 3.16 kV while that for N_2 (50 slm)/O_2 (200 sccm)/SF_6 (2.5 slm) was 2.7 kV, therefore, a lower turn-on voltage was obtained by adding 2.5 slm of SF_6. The consumed power for N_2 (50 slm)/O_2 (200 sccm)/SF_6 (2.5 slm) was 2330 W while that for N_2 (50 slm)/O_2 (200 sccm) was 1119 W. Therefore, the addition of 2.5 slm of SF_6 increased the power consumption in the plasma by ionizing and dissociation the gas mixture further possibly through the penning ionization and dissociation. At N_2 (70 slm)/ O_2 (200 sccm) + SF_6 (3 slm), the maximum PR etch rate of about 1850 nm/min could be achieved.

PS-ThP18 SiO_x Thin Films Deposition by using a Modified Pin-To-Plate Dielectric Barrier Discharge Source in Atmospheric Pressure, ***E.L. Gil**, J.B. Park, J.S. Oh, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

SiO_2 films are used in various areas due to the excellent physical and chemical properties such as optical transparency, chemical inertness, scratch resistance, and sufficient hardness. In this study, as an application to a thin film passivation layer for flexible substrates, the deposition of SiO_2 thin film has been investigated. Especially, for the in-line and the roll-to-roll processing of flexible substrate, SiO_2-like thin film was deposited by an atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) technique at atmospheric pressure and at room temperature. A modified dielectric barrier discharge (DBD) called a "pin-to-plate-type DBD" having the combined characteristics of the remote-type DBD was used with a gas mixture of hexamethyldisilazane (HMDS)/O_2/He/Ar in order to generate high-density plasmas and to limit the damage to the substrate. The characteristics of SiO_2-like thin film were varied with gas mixture. As HMDS flow rate was increased, higher -$(CH_3)_x$ bonds and lower -OH bonds were obtained due to the decreased recombination of carbon or hydrogen with oxygen, and consequently more particles and rough surface were observed. Although the increase of oxygen in the plasma was beneficial in removing all impurities relating to carbon, further increase of O_2 more than 14 slm obstructed forming the pure SiO_2-like films resulting in a rough surface. By using a gas mixture of HMDS (150 sccm)/O_2 (14 slm)/He (5 slm)/Ar (3 slm), SiO_2-like thin films with a low impurity could be obtained at a deposition rate of approximately 42.7 nm/min.

PS-ThP19 Studies of the Metal Electrode Erosion by Microplasmas in Saline Solution, ***C.Y. Sie**, C.L. Chen, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

The studies of the erosion of metal electrode by microplasmas in saline solutions are preformed. The plasma is ignited in saline solution of concentrations ranging from 0.01 to 2 M . This plasma is sustained by a DC power source with the voltage up to 600 V or a AC power source with the same voltage range and the frequency between 50 ~ 1000 Hz. The electrode on which the plasma is ignited is a metal electrode covered 0.5 mm in diameter by an alumina tube to precisely define the length exposes to the solution. The erosion of tungsten, titanium, and platinum electrodes is studied. During the plasma processing, the electrode erosion appears to be inevitable. It is found that when tungsten is used as the electrode, the most severe erosion occurs when the electrode is positive biased with the applied voltages at which no plasma is ignited, suggesting the electrolytic reaction plays an important role in the electrode erosion. With the plasma ignited at a higher applied voltage, increase in the applied voltage leads to a decrease in the erosion rate. When the AC power source is used, the erosion rate increases with the power frequency. In this presentation, the major erosion mechanism will be proposed and the strategy how the erosion rate can be minimized will be presented.

PS-ThP20 Formation of Size Regulated Platinum Nanoparticles Synthesized by Solution Plasma Process, ***T. Ishizaki***, AIST, Japan, *N. Saito, O. Takai*, Nagoya University, Japan

Platinum nanoparticles have been applied to high activation of photo catalysis, catalysis for fuel cells, and cosmetics. Platinum nanoparticles have been synthesized by various techniques including chemical reduction, photo reduction and electrochemical technique. However, in these techniques, it takes few hours to synthesize the nanoparticles or chemically toxic substances leave in a product. Thus, it is required to develop an environmentally friendly technique to synthesize nanoparticles. We have developed 'Solution Plasma', which is defined as plasma in aqueous solution. Solution plasma has attracted much attention as a novel chemical reaction field. As solution plasma generates UV light, electrons, and radicals, it would reduce metal ions to nanoparticles without reduction agents. In this study, we aimed to synthesize platinum nanoparticles by solution plasma. In addition, we investigated influence of solution pH on the sizes of the platinum nanoparticles. Optical absorption of nanocolloidal platinum was measured by UV-vis spectrometer. The nanoparticles were observed by transmission electron microscopy (TEM).

$H_2PtCl_6 \cdot 6H_2O$ (1.44mM) and PVP (Polyvinylpyrrolidone, 12.1mM) were used as row materials. The pH of solution was varied from 2.5 to 4.5. The electrical conductivity was adjusted to 1.5μS/cm by the addition of KCl. A pulsed power supply was utilized to generate plasma. Pulsed voltage of 1.6kV was applied between the tungsten electrodes in the solution. Pulse width and frequency were varied from 2.0 to 3.0μs, respectively.

Solution color changed from orange to dark brown at discharge times of more than 40 min. An absorption peak at 262 nm originated from $PtCl_6^{2-}$ became weaker with the increases of the discharge time, while baselines in the spectra became higher in all the range. These results indicate the formation of platinum particles. TEM image shows that the mean diameter of the nanoparticles was 10nm. Debye rings by (111), (200), (220), (311) were also observed by diffraction patterns. The effects of pulse width, frequency and pH on the particle size distribution were also discussed.

PS-ThP21 Effects of Dirty Walls on the Plasma Potential of a Multi-Dipole Chamber, ***J.P. Sheehan**, N. Hershkowitz*, University of Wisconsin-Madison

In a multi-dipole chamber with dirty walls, the plasma potential is observed to be negative with respect to grounded wall in the tens of volts. The plasma is generated by hot filaments releasing monoenergetic primary electrons ranging from 35 to 60eV. The primaries can exist in significant concentrations relative to the plasma electrons (up to 0.5% primaries as measured by a planar Langmuir probe) and contribute to charge neutrality, but not significantly to current balance. It is observed that the plasma potential becomes more negative with increasing relative concentrations of primary electrons. The potential profile next to the wall was measured using an emissive probe in the limit of zero emission[1]. The negative potential in the bulk plasma drops an additional few Te radially to the wall. The radial and axial potential profiles resemble those found in a chamber with clean walls and a positive plasma potential except the entire profile is shifted 10 – 20V lower. Possible mechanisms for these observations are suggested.

References

[1] J. R. Smith, N. Hershkowitz, and P. Coakley, Rev. Sci. Instrum. **50**, 210 1979.

PS-ThP22 New Solutions for Magnetron Sputtering Technology, ***M. Cichowlas***, Huettinger Electronic, Poland

Traditionally, DC-pulsed units are advised to number of applications like: AZO, reactive sputtering with SN target, etc. This recommendation is based on the assumption that a DC-pulsed unit is enough to match process requirements.

Typical recommendations for usage of DC-pulsed units are as follows:

- high ARC rate,

- reactive process (reactive gas in the chamber),

The aim of this article is to introduce DC-non pulsed and High-Power (HIPIMS) units as more interesting alternative for expensive DC-pulsed units.

1. DC no-pulsed units

Advanced, powerful functions implemented into DC-non pulsed units, gives beneficial solution for processes affected by highly arcing materials like AZO. Ability to stable operation with extremely highly arcing frequency is one of most interesting features of DC power supplies developed by Huettinger Electronic. Mentioned units are able capably to work with 8000 ARCs/sec with 60kW output power.

Fig. 1. Behavior of AZO - extremely high arcing rates-70.000 arcs/s.

2. HIPIMS units

The other potentially interesting technique is HIPIMS coating. Looking for DC pulsed or DC non-pulsed processes, HIPIMS is going to serve fully dense, defect free films. Additionally, HIPIMS process leaves substrate temperature at lower level, compared to DC units. This gives a possibility for usage of completely new materials to be coated, like polymeric, foil or rubber. Moreover, power supplies for HIPIMS applications are equipped with CompensateLine (cable length compensation circuit), this allows to reduce arc energy to 0,3mJ.

Fig. 2. Behaviour of HIPIMS unit with arc during a HIPIMS pulse.

DC non-pulsed units can be used for advanced reactive processes, efficiently competing with DC pulsed units. The HIPIMS gives new possibilities for fully dense films on material required substrate temperatures.

Plasma Science and Technology
Room: Aztec - Session PS-FrM

Liquids and Multiphase Discharges
Moderator: C. Labelle, GLOBALFOUNDRIES

8:20am **PS-FrM1 Dynamic of Plasma Ignition and Propagation in Water**, *W.G. Graham,* Queen's University Belfast, Northern Ireland, ***A. Rousseau****, P.H. Ceccato, O. Guaitella*, Ecole Polytechnique, France **INVITED**

We present an experimental study of a filamentary microplasma discharge inside liquid water. Such plasmas are used for liquid electrical insulations tests and for pollution control of water [1-2]. It was recently shown that the propagation velocity was found to be surprisingly constant whatever the experimental parameters and especially as a function of the water conductivity [3]. The purpose of the present work is to understand the physical mechanisms responsible for initiation and propagation of the discharge. A point to plane electrode configuration submerged in water has been constructed and was submitted to a high voltage pulse. Filaments inception and propagation and several discharges modes have been characterized with electrical measurements and time resolved nanosecond imaging. A Shadow diagnostic using 2 fast cameras was implemented to study the gas content and the shock wave emission from the discharge. The influence of the applied voltage polarity and the water conductivity was investigated. At positive high voltage the growth of the discharge begins by the nucleation of a microbubble at the needle electrode within a few microseconds at an applied voltage of 40kV, a hemispheric branching filamentary structure grows at 3km/s during 100ns and is followed by the propagation of second filamentary structure ten time faster. This continuous propagation on a nanosecond time scale is followed by a stepwise propagation in case of distilled water. When the filaments reach the opposite electrode electrical breakdown occurs. At negative polarity the discharge is much slower 600m/s. The morphology of the gas cavity is driven by interface instability.

[1] P. Bruggeman et al. 2009, J. Phys. D: Appl. Phys. 42

[2] B. R. Locke et al. Ind. Eng. Chem. Res. 45 882-905

[3] P. Ceccato et al. J. Phys. D: Appl. Phys. 43 (2010) 175202

9:00am **PS-FrM3 Copper Nanoparticles Synthesized by Glow Discharge in Solution**, ***N. Saito****, Y. Aoki, J. Hieda, O. Takai*, Nagoya University, Japan

Plasma in gas phase is widely used in many industrial fields such as electronic device manufacturing processes (plasma etching, sputtering, plasma-enhanced CVD, etc.), hard coating processes (ion plating, sputtering, etc.), surface treatment processes (low or atmospheric pressure plasma treatments, sputtering, plasma etching, etc.) and so on. Plasma in solid phase has been utilized finally for surface plasmon resonance (SPR) spectroscopy, nanoparticles, etc., and plasmonics is developing as a new research field. On the other hand, plasma in liquid phase is not generally well-known, although it has been partially utilized in water treatments and electrical discharge machining. The fundamentals of plasma in liquid phase have not been established, including its generation techniques, its state, and activated chemical species. However, it would be reasonable to expect a higher reaction rate under lower-temperature conditions, and the greater chemical reaction variability since the molecular density of liquid is much higher than that of gas phase. So we have named the plasma in liquid phase "solution plasma" because we make variety of plasma by choosing the combinations of solvents and solutes in solutions, and are developing solution plasma processing (SPP). In SPP, aqueous solutions, nonaqueous ones, liquid nitrogen, supercritical fluids, etc. can be utilized as solutions. Recently, we have investigated the features of SPP and the applications such as syntheses of nanoparticles and mesoporous silica, and surface modification of particles.

In this research, copper nanoparticles were synthesized by a glow discharge in solution. A pulsed power supply was used to generate discharges. The pulsed width was 2 micro seconds, the repetition frequencies were 10 – 15 kHz. The electrode was tungsten wire in the diameter of 1 mm with electrode gap of 0.3 mm. Ethanol was used as a solution. Monohydroxy copper acetate (II) was utilized as a raw material of copper. The molar concentration of raw material was adjusted to 5mM. Moreover sodium iodide was added to the solution up to 5 mM. The solution and the productants after the discharge were analyzed by 1H NMR, Uv-Vis spectroscopy, XRD, TEM. Finally, TEM showed the synthesis of copper nanoparticles. Moreover 1H NMR show the presence of acetaldehyde in the solution after discharge, which might work as a reducing agent.

9:20am **PS-FrM4 The Consequences of Bubbles in the Electrical Breakdown of Liquids**, ***N.Yu. Babaeva****, M.J. Kushner*, University of Michigan, Ann Arbor

Streamer discharges in liquids do not likely directly develop through the liquid phase. It is thought that breakdown occurs inside bubbles where streamers preferentially propagate along the surface of the bubbles and near gas–liquid interfaces [1]. In many applications, plasmas are intentionally generated inside bubbles in liquids to produce reactive species which then diffuse through the gas-liquid interface. For short (nanoseconds) time scales, one of the proposed mechanisms for electrical breakdown in liquids is the sequential linking of plasmas in bubbles (PBs). For example, the large E/N produced in the bubble compared to the adjoining liquid enables more rapid breakdown and charging of inner surfaces. If the bubbles are in favorable alignment, the inter-bubble electric field enhancement may provide a mechanism for propagating the streamer through the liquid. On longer timescales (microseconds) when heating of the gas-liquid interface becomes important, thermally induced breakdown likely occurs. The mechanism includes heating and evaporation of adjacent liquid layers, expansion of the gas phase accompanied by the deformation of the gas-liquid interface by electrical forces. In this case the favorable alignment of bubbles does not play an important role.

In this paper, properties of PBs and of streamers intersecting with liquids will be discussed based on results of computer simulations.[2] The model used in this investigation is *nonPDPSIM*, a 2-dimensional plasma hydrodynamics model in which the densities and momentum of charged and neutral particles are solved coincident with Poisson's equation and radiation transport. On short time scales liquids are computationally treated in the same manner as plasma with an appropriate density dependent polarization to provide the liquid density permittivity. On longer time scales, heating and evaporation of the adjacent portions of the liquid is addressed.

We will also address streamers intersecting with liquids in the context of plasma treatment of biological tissue or wounds. In this case the intersection of streamers with the liquid on time scales shorter than the dielectric relaxation time additionally produce electric fields within the underlying tissue. The values of these electric fields, as large as 100s kV/cm, are above the threshold for breakdown for atmospheric pressure gas bubbles or gas filled vacuoles. As such, it may be possible to produce plasmas below the surface of the liquid or within tissues.

[1] P. Bruggeman and C. Leys, J. Phys. D **42,** 053001 (2009).

[2] N. Yu. Babaeva and M. J. Kushner, J. Phys. D **42**, 132003 (2009).

* Work supported by the Department of Energy Office of Fusion Energy Sciences

9:40am **PS-FrM5 Diagnostic Studies of AC-driven Plasmas in Saline Solutions: the Effect of the Frequency on the Plasma Behavior**, ***H.W. Chang****, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Plasmas in saline solutions receive considerable attention in recent years. How the electrical power frequency influences the plasma behavior remains unclear. In this presentation, diagnostic studies of plasmas ignited in saline solution driven by an AC power source are presented. An AC power source with tunable frequencies between 50~1000 Hz and a voltage up to 600 V is used. The electrode at which the plasma is ignited uses a Pt wire 0.5 mm in diameter covered by a glass tube to precisely define the area exposes to the solution. Saline solutions with concentrations 0.01 M ~ 2 M are used. Diagnostic tools used include a voltage and a current probe to monitor the electrical characteristics. A high speed camera with a frame rate up to 1200 frames/sec is used to capture the bubble and plasma dynamics. An optical emission spectrometer and a photomultiplier tube are used to monitor the optical emission emanating from the plasma. It is shown that the plasma behavior is strongly coupled with the bubble dynamic adjacent to the electrode tip. Two distinct modes, namely the static mode and the jetting mode, are identified. In the static mode, a bubble with a diameter 1~ 3 mm is attached at the electrode tip for many seconds. The oscillation of the bubble is found to be relevant to the plasma behavior and is partially responsible to the stability of the discharge. This mode occurs mostly at the frequency below 100 Hz. The jetting mode occurs at a frequency higher than 300 Hz. In this mode, the plasma is ignited intermittently and is less stable comparing with the bubble mode. Under low applied voltages, bubbles of hundreds of μm in diameter are continuously jetted from the electrode tip. As the applied voltage increases, the micro-bubbles tend to coalescence into large bubbles and attach back to the electrode thus the switching of the above two modes is observed. Further increase in the applied voltage leads to bright plasmas with high current and severe

electrode damage occurs. It is also observed that under the applied voltage above 200 V, the plasma ignited in the negative half cycle of the power period shows a much stronger emission intensity than that in the positive half cycle. By the integration of the high speed image, the optical emission spectroscopy, and the electrical characteristics, the mechanism of the plasma formation under various frequencies and how it is affected by the bubble dynamics will be proposed.

10:00am **PS-FrM6 Solution Plasma Processing of Carbon Nano-Fillers in Ammonia Aqueous Solution for Preparation of Polymer Nano-Composite Materials**, ***T. Shirafuji***, *Y. Noguchi, J. Hieda, N. Saito, O. Takai*, Nagoya University, Japan

Solution Plasma Processing (SPP) has been performed in ammonia aqueous solution for amino functionalization of multi-walled carbon nanotubes (MWCNTs). The MWCNTs, which do not disperse in aqueous solution, have uniformly dispersed after the SPP. The treatment time for obtaining 10 g of the well-dispersed MWCNTs was only 2 hours. Infrared absorption spectroscopy of the SPP-treated MWCNTs revealed that NH_2 bonds were formed on the MWCNTs. The destruction of the MWCNT structure was not observed as shown by the characteristic Raman spectrum. The composite materials were prepared with the SPP-treated MWCNTs and polyamide 6 (PA6), and showed better tensile, bending and impact strength than those of non-treated MWCNTs and polyamide 6. Grafting of the ε-aminocaproic acids has been performed on the NH_2 sites of the MWCNTs. Appearance of the amide-I and amide-II bands in the infrared absorption spectrum of the grafted sample indicated that the grafting was successfully achieved. By grafting the ε-aminocaproic acids, which has the molecular structure of one segment of the PA6, we can expect hydrogen bonding between the N-H and O=C sites in the PA6 and grafted epsilon-aminocaproic acids, and can expect further improvement in mechanical strength of the PA6/MWCNT composites.

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