Plasma Science and Technology
Room 302 - Session PS-MoM

Plasma Diagnostics

Moderator: S.G. Walton, US Naval Research Laboratory

9:00am **PS-MoM3 Emissive Probes in Processing Plasmas - A Good Way to Measure the Plasma Potential***, **N. Hershkowitz**[1], D. Lee,* University of Wisconsin **INVITED**

Electron emissive probes can provide measurements of the plasma potential with potential resolution of 0.1 V and spatial resolution of 0.1 cm in low pressure DC Argon plasma. The plasma potential is an important parameter in processing plasmas. However, such plasmas present many challenges to the use of emissive probes including rf, reactive gases, plasma deposition, impurity generation and relatively high neutral pressure so probes are rarely used. This talk provides experimental evidence that many of the challenges can be overcome and argues for increased use of emissive probes.

9:40am **PS-MoM5 A New Diagnostic Method of Radio-Frequency Plasmas Produced in Insulated Vessels***, **H. Shindo**,* Tokai Univeristy, Japan

A new method to measure electron energy by an emissive probe has been proposed. The method is based on measurement of the functional relationship of the floating potential and the heating voltage of emissive probe. From the measured data of the floating potential change as a function of the heating voltage, the curve of the probe collection current-voltage can be analytically obtained. The present method has several important advantages of the following: (1) it is even applicable to radio-frequency plasma in which the potentials are usually fluctuating, (2) also applicable to plasmas which are produced in non-conductive containers. In the experiment, the emissive probe 30 micrometer diameter tungsten was heated by 40 kHz pulse voltage, and the floating potential at the heating voltage off period and the floating potentail difference between the heating off and on period were measured by digital oscilloscope in argon plasma. The measurements were made in both the capacitively coupled and inductively coupled plasmas. It was shown that the plasma electron energy probability function could be obtained without any RF compensating circuit even in capacitively coupled plasmas. In particular, since the method is very sensitive near the plasma potential, the clear indication for the depletion of the low energy electron could be obtained. This low energy electron depletion is due to high plasma potential. Therefore, in the inductively coupled plasma this low energy electron depletion was obtained near the induction antenna, but at the further positions from the antenna the energy distribution became Maxwellian. This feature has also been reported recently. This change in the electron energy distribution found in ICP was very systematic with the gas pressures and the distnaces from the antenna. Thus the present method is quite innovative in that it is applicable to the potential fluctuating RF plasma and measurements are all done in a floating condition of probe.

10:00am **PS-MoM6 Energy Dissipation in Capacitively Coupled Discharges of Molecular Gases***, **G.F. Franz**,* Munich University of Applied Sciences, Germany

The heating of heavy plasma components by elastic collisions with electrons is one of the main mechanisms of energy transfer to ions and neutrals at low and medium power input, but often regarded inevitable. It is measured by optical emission spectroscopy, employing rovibrational bands of nitrogen, which is doped to capacitively coupled discharges of hydrogen and chlorine, and for comparison, also argon.@footnote 1,2@ The temperatures in chlorine are comparable to the inert gas argon, whereas hydrogen is significantly cooler, but all three will saturate at higher power inputs (more than 1/4 W/cm@super 2@ absorbed power density or at dc bias values higher than about 600 V). It is this region where parasitic processes (the most prominent is power absorption by ions in the sheath) will begin reducing the phase angle of power input from nearly perfect -90° to values of less than -20°. These data is discussed in terms of the functional dependence of electron density and electron temperature on discharge pressure and power input which have been recorded earlier.@footnote 3,4@ @FootnoteText@ @footnote 1@ M. J. Schabel, V.M. Donnelly, A. Kornblit, and W.W. Tai. Determination of Electron Temperature, Atomic Fluorine Concentration, and Gas Temperature in Inductively Fluorocarbon/Rare Gas Plasmas Using Optical Emission Spectroscopy, JVST A 20, 555 (2002)@footnote 2@ B. Bai and H.H. Sawin: Neutral Gas Temperature Measurements within Transformer Coupled Toroidal Argon Plasmas; JVST A 22, 2014 (2004)@footnote 3@ G. Franz: Comprehensive Analysis of Capacitively Coupled Chlorine-Containing Discharges, to be published in JVST A, May/June 2005@footnote 4@ G. Franz, M. Klick: Electron Heating in Capacitively Coupled Discharges and Reactive Gases, to be published in JVST A, 2005.

10:20am **PS-MoM7 Spatial and Temporal Measurement of Electric Fields in a Plasma***, **E.V. Barnat**,* Sandia National Laboratories

We employ laser-induced dip-fluorescence to detect Stark shifts of atomic argon Rydberg states induced by electric fields present in the plasma sheath. The choice of the probed Rydberg state determines the electric field range and resolution we can achieve. Using the experimentally calibrated behavior of the Rydberg levels, both spatially and temporally resolved maps of the electric fields are obtained above powered electrodes generating a plasma. Electric fields around a technologiclly relevant electrode are mesured and compared to fields measured around simplified electrode structures. Both maps of the electric fields as well as excition and ionization profiels around the electrode demonstrates how the surfaces couple to the plasma. @FootnoteText@ This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram 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.

10:40am **PS-MoM8 Modified Actinometry for Monitoring Atomic Radicals in Molecular Gas Discharge***, **T. Ishijima**, T. Okada, Y. Tanabe, H. Sugai,* Nagoya University, Japan

Actinometry technique has widely been used for detecting radicals in processing plasmas owing to its simplicity. There are many arguments on its reliability, especially from a viewpoint of electron-impact excitation processes. For example, one often encounters a serious difficulty in detecting atomic radical X in a discharge in diatomic molecule gas X@sub 2@: the dissociative excitation of X@sub 2@ induces the same optical emission line with the direct excitation of X, so that a standard actinometry taking the optical intensity ratio between actinometer (say, Ar) and the radical does not give the direct information of the radical density. Here we propose a method to discriminate a direct excitation component in the actinometry. This method is successfully applied to monitoring the N atom and the O atoms in high-density plasma nitridation and oxidation of silicon surface at low temperatures, respectively. The relative atomic densities obtained in the modified actinometry are compared with the absolute densities measured by appearance mass spectrometry. Preliminary measurements were applied in the the microwave excited plasmas of 2.45 GHz at 0.3 - 1.0 kW. The relative N atom densities are evaluated with N@super 4@P intensity (821 nm) normalized by Ar@super 2@P intensity (750 nm). When the pressure increases from 50 mTorr to 300 mTorr, both the absoulte N atom density and relative atomic densities increase monotonously in the same condition for input power and mixing ratio of Ar/N@sub 2@=9/1. Correlation with the measured atomic densities with the surface analysis data is discussed.

11:00am **PS-MoM9 Rare Gas and O Metastable Density in Rare Gas Diluted Oxygen RF Plasmas***, **T. Kitajima**,* National Defense Academy of Japan, Japan*; K. Takahashi, T. Nakano,* National Defense Academy of Japan*; T. Makabe,* Keio University, Japan

Rare gas diluted O2 plasmas are interested for application to high quality SiO2 film formation. Especially, metastable O(1D) atoms produced in rare gas diluted O2 plasma is believed to promote higher production rate of the oxide films. The density of rare gas metastable atoms and O metastable atom in rare gas diluted O2 radio frequency (RF) capacitively coupled plasma (CCP) was measured by optical absorption spectroscopy (OAS). By decreasing O2 fraction in plasma, O(1D) metastable density icreases to twice of pure O2 plasma at 100 mTorr. Decreases of rare gas metastable densities due to addition of O2 indicate efficient O atom production by rare gas metastables via collisional quenching. Krypton metastable had highest density among four rare gas species for fixed RF power. The decrease of Ar metastable density due to O2 addition showed quantitative agreement with reported quenching rate coefficient. Detailed discussion on different gas pressures illustrates reduced O2 fraction is the key for selective production of O atoms through rare gas metastables.

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[1] **2004 Plasma Prize Winner**

11:20am **PS-MoM10 Prediction of Plasma UV Radiation Damages Using On-wafer Monitoring Sensors***, **Y. Kato**, Y. Ishikawa, M. Okigawa, S. Samukawa,* Tohoku University, Japan

We have proposed a simple on-wafer monitoring sensor for prediction of UV and VUV photon radiation damages. In this sensor, the electrical currents were induced in the dielectric film and they could be measured by the plasma radiation. We first found that the current was completely corresponding to the generation density of hole-electron pairs in dielectric films and to the increase in interface state at the interface between the dielectric film and silicon under plasma irradiation. In this paper, the relationship between the induced electrical current in the sensor and plasma discharge conditions was investigated to predict the UV radiation damages. The dependence of the induced currents in the sensor on the plasma generation power, discharge pressure and gas flow rate was evaluated. Based on these results, we found that the UV radiation damages could be predicted and the low damage processes could be proposed for plasma etching processes.

11:40am **PS-MoM11 Sheaths and Pre-sheaths in Collisionless and Collisional Active Plasmas: Planar and Cylindrical Probes***, **F. Iza**, J.K. Lee,* Pohang University of Science and Technology (Postech), S. Korea

Ion kinetics in the sheath and pre-sheath of planar and cylindrical probes have been studied by means of particle-in-cell computer simulations. Low temperature argon discharges with Maxwellian electrons have been simulated in collisionless and collisional regimes. As pressure increases, the sheath, i.e. the region of positive space charge surrounding the probe, becomes collisional and the velocity of the ions entering the sheath falls below the Bohm velocity (u@sub B@). For planar probes, ions enter the sheath with a velocity given approximately by u@sub B@(1+4@lambda@@sub D@/@lambda@@sub i@) where @lambda@@sub i@ is the ion mean free path and @lambda@@sub D@ the Debye length at the sheath edge. This relation differs from that given in@footnote 1@ because the electric field boundary condition at the sheath edge used in@footnote 1@ corresponds to a field reached well inside the sheath. For a floating planar probe, the voltage drop across the sheath increases with pressure to balance the electron and ion fluxes and the ion flux is almost independent of pressure despite the variations in ion velocity. As observed experimentally,@footnote 2@ simulation results show that the voltage across the presheath can be significantly larger than half electron temperature. For planar probes, this voltage depends non-linearly on the electron temperature and increases rapidly for electron temperatures below 2eV. For cylindrical probes, however, the voltage across the presheath can be drastically reduced by the geometrical increase of current density as ions approach the probe. The floating potential and the ion velocity at the sheath edge decrease with decreasing probe radius and for thin probes (r@sub p@<@lambda@@sub D,i@), the voltage drop across the presheath is negligible (<<0.5T@sub e@). @FootnoteText@ @footnote 1@ V A Godyak and N Sternberg, IEEE Trans. Plasma Sci. 18 (1990) 159-168.@footnote 2@ L Oksuz and N Hershkowitz, Plasma Sources Sci. Technol. 14 (2005) 201-208.

Plasma Science and Technology
Room 302 - Session PS1-MoA

Dielectric Etch I

Moderator: H. Maynard, IBM

2:00pm **PS1-MoA1 Reduction of Line Edge Roughness for 65nm Technology Node for Etched Contact Holes*, B. Goodlin,*** *D. Farber, T. Lii, G. Shinn,* Texas Instruments Incorporated

For the 65nm technology node, reduction of contact hole line edge roughness is critical for reliable performance in densely packed memory cells. Origins of contact line edge roughness are attributable to three different mechanisms: 1) pattern transfer line edge roughness, resulting from propagation of striations from 193nm resist to the underlying substrate, 2) deposition-related line edge roughness, resulting from pattern transfer of non-uniform and irregular shaped deposition at the top of the hole to the bottom of the etched feature, and 3) pin-hole punch-through line edge roughness, where faceting or thinning of resist towards the end of etch processing results in shallow pin-holes that do not propagate down the entire length of the feature being etched. In order to fully appreciate these different types of line edge roughening for process optimization, a metrology technique was utilized that could characterize roughness at both the top and bottom of an etched feature. Using such metrology, an etch process has been optimized to minimize line edge roughness, while satisfying several other strict processing constraints.

2:20pm **PS1-MoA2 Difference in Etch Depth between Isolated and Dense Holes in Via-Etching of SiOC Film*, Y. Momonoi,*** Hitachi, Ltd., Japan*; K. Yonekura,* Renesas Technology Corp.

Carbon doped silicon oxide (SiOC) has been widely used in integrated circuits (ICs) in order to reduce the total resistance capacitance (RC) delay in the interconnects. However, we found that there was a significant difference between the etch depths of isolated and dense SiOC via-holes. In addition, we found a mutually opposite dependence of etch depth on pattern density under different etching conditions. Equally, the etching properties, e.g., etch rate and depth of unexpected etch stop that are dependent on pattern density were different in different etching conditions. We expect that the difference in etch depth is a key issue in controlling critical dimensions, mask selectivity, and erosion of etch stop layers. In investigating the difference, it was clarified that the etch depth of isolated patterns was deeper than that of dense patterns when the etch depth was determined by an unexpected etch stop (narrow etch-stop-margin condition), and that the etch rate of isolated patterns was slower than that of dense patterns when the etch depth was based on etch rate (wide etch-stop-margin condition). We also found that the difference increased the longer the wafers were stored, which is in accordance with an increase of a gas degassed from SiOC in thermal desorption spectroscopy. We therefore investigated the influence of the gas on SiOC etching by adding it to plasma. Consequently, the added gas resulted in the same difference in etch depth as the difference that occurred between isolated holes and dense holes in both etch-stop-margin conditions. These results indicate that more of the gas degassed from isolated holes in SiOC determines the difference in etching depth.

2:40pm **PS1-MoA3 Etching Mechanisms of Low-k Material with the Solid First@superTM@ ILD Process in Fluorocarbon based Plasma*, T. Chevolleau,*** *D. Eon, M. Darnon, L. Vallier, O. Joubert,* CNRS/LTM, France

In CMOS technology, most of the interlayer dielectric materials achieve low k value by introducing porosity in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. However, porous materials as pSiOCH are very sensitive to ash and etch plasma exposure and one of the integration challenges is to reduce the impact of these plasma processes. To solve this issue, one of the emerging solutions is the Solid First@superTM@ ILD process. In this approach, the porosity in SiOCH is generated by releasing porogens (carbon based polymer) after patterning or copper filling. The SiOCH containing porogen materials are expected to behave like non-porous materials during the etching and ashing processes (as long as the porogens have not been released). This study concerns the etch mechanisms of a solid first SiOCH low-k (Zirkon V8@super+@ from Rohm and Haas) and selectivitiy to SiC and SiCN etch stop layer. The etching is performed on blanket wafers in an industrial MERIE reactor (Magnetically Enhanced Reactive Ion Etcher) using fluorocarbon based plasmas. Etch rates are measured by ellipsometry, chemical surface composition is analyzed by quasi in-situ XPS, and bulk modification by infrared spectroscopy. Etching is performed in fluorocarbon based plasmas (CF@sub4@) in mixture with Ar, CH@sub2@F@sub2@, or O@sub2@). Similarly to dense SiOCH materials, the etch rate decreases with either increasing Ar dilution or polymerizing gas addition. Nevertheless, XPS analyses reveal that the increased carbon content in the low-k material due to the presence of the porogen leads to the formation of a thick fluorocarbon overlayer during plasma exposure. Consequently, etch stop phenoma can occur even with low polymerizing fluorocarbon plasmas. On the other hand, FTIR analyses clearly show that the presence of porogens in the SiOCH matrix prevent bulk modification during a fluorocarbon plasma exposure.

3:00pm **PS1-MoA4 The Role of Inert Diluents in Low Pressure Electronegative Fluorinated Gas Discharges under Dual Frequency Excitation*, M. Hussein,*** *M. Abdelrahman,* Intel Corporation

We investigated the role of argon (Ar) and helium (He) dilution on the discharge characteristics and etch rate performance of NF3 plasma under single and dual excitation frequency conditions. The discharge complex impedance was measured using an advanced, passive I-V probe installed between the match network and the bottom electrode of a dual frequency, fixed gap, capacitively-coupled parallel plate commercial etch system. We studied the relationship between the etch performance of NF3/Ar/He plasma and the discharge complex impedance and dissipated power. A 300mm diameter test wafer substrate, with ~3-5% of its surface area occupied by vias patterned into a 360nm thick carbon-doped oxide (CDO) deposited on top of a 300nm silicon carbide (SiC) layer, was utilized for etch rate characterization. Both the CDO and SiC films were exposed to the plasma and etched at the same time, mimicking the process of SiC barrier etch used at the end of a dual damascene patterning process flow. We varied the NF3 flow rate form 0 to 18% of the total flow over a pressure range from 10mT to 150mT. Under dual frequency excitation, where 400Watts 60MHz and 50 Watts13.56MHz were applied to the top and bottom electrodes, respectively, the discharge complex impedance changed drastically over the tested pressure range. Below 40mT, the discharge is characterized by low impedance (~10-20 ohm). As the pressure increases, the impedance increases and reaches an asymptote at the 20-25 ohm range. This general trend was not observed under the 13.56MHz single frequency excitation mode, where a monotonic decrease in impedance with increasing pressure was observed regardless of diluents. We propose a model, similar to Langan's et al.,@footnote 1@ suggesting that the dominant role of the diluent in NF3 plasmas is to control the electronegativity of the discharge, and thus to control real power dissipation. @FootnoteText@@footnote 1@J. Langan, S. Beck, B. Felker and S. Rynders, J. Appl. Phys. 79(8), pp.3886, 15 April 1996.

3:20pm **PS1-MoA5 Polymer Management in Dielectric Etch*, E.A. Hudson,*** *A. Marakhtanov, K. Takeshita,* Lam Research Corp. **INVITED**

Etching of dielectric films for microelectronics requires processes which provide control of feature profiles and high selectivity to mask and stop layer films. For most dielectric films, especially Si-containing materials, plasma etch processes tend to deposit fluorocarbon or hydrofluorocarbon films. These polymeric films play many essential roles, acting to passivate feature sidewalls, to control critical dimensions and profile angles, to reduce mask loss, to minimize corner faceting, and/or to protect underlayers. But polymer deposition on reactor surfaces can lead to difficulties in maintaining stable reactor conditions. This paper focuses on several critical areas in dielectric etch processing where understanding and managing the behavior of deposited polymer is crucial. One focus is the effect of polymer upon microscopic structures. For example, low-k dielectric films tend to be modified by photoresist removal processes. Protective sidewall films have shown the capability to limit strip-induced damage. In another example, fluorocarbon films prepared under simulated conditions for sidewall vs top surfaces have shown different properties. These differences can influence final etch profiles. Another focus is the behavior of polymer on reactor surfaces. Multi-step in-situ processing has become a standard production method for reducing cost and cycle time. To maintain a stable process, it is important to understand how the chamber condition evolves during the sequential etch steps, and to minimize the interaction between these steps. Several process and plasma parameters influence the measured deposition rate of polymer on reactor surfaces. For transitions from a polymerizing step to a step which can etch polymer, the plasma conditions and process results may be influenced by the removal of residual chamber polymer. Time-resolved plasma measurements show the extent of this step-to-step chamber memory effect, and how it can be minimized.

4:00pm **PS1-MoA7 Polymer Management in Advance Dielectric Etch Applications**, ***G.A. Delgadino***, *D. Buchberger, Y. Zhou, Y. Xiao,* Applied Materials, Inc.

Historically, dielectric etch has rely on polymer deposition to achieve desire selectivity to photoresist and barrier film. As features size shrinks, softer shorter wavelengths photoresist are required. In particular, 193nm PR is not only thinner but also more prone to form veils and striations. Heavy polymer deposition is usually used to protect Photoresist and to minimize pinhole formation and striations. Unfortunately fluorocarbon deposited on the wafer and the chamber is released during insitu ashing attacking the barrier layer and sidewall. In this paper we describe the development of a polymer rich recipe that greatly protects photoresist resulting in no top view striation. Minimal barrier loss can be achieved by depositing a thin polymer film over the barrier minimizing barrier loss during ashing. Polymer also deposits in undesired places like the back side of the wafer. Small gaps allow polymer precursors to diffuse in but prevent the ashing plasma to rich the same spots. This deposited polymer might flake during other wafer processing steps reducing yield,@footnote 1@ or might just contaminate other process equipment like the PVD preclean chamber increasing frequency of maintenance. In this work we evaluate intra-chamber and intra-system solutions compatible with low k porous films, to minimize yield loss related to such undesired deposition. @FootnoteText@ @footnote 1@ T. Dalton et. al. AVS 2004.

4:20pm **PS1-MoA8 Analysis and Impact of F Penetration into low-k Dielectrics during Plasma Etch**, *R. Augur,* ***C. Labelle***, Advanced Micro Devices Inc.*; C. Parks, S. Mehta, N.C.M. Fuller,* IBM Corporation

The semiconductor industry's move towards incorporating porous low-k dielectrics in future technology generations raises many questions about the thermal, mechanical, and chemical interactions between porous dielectrics and the different environments they will encounter during integration. This paper reports detailed analysis of F penetration into porous and dense SiCOH-based low-k dielectrics, introduced during plasma etch. SIMS depth profiling was used to compare the concentration of F in etched and non-etched regions. For porous materials, the F concentration was found to be approximately 5 times higher in via-etched regions, and lateral penetration occurred throughout the thickness of 300nm films. Profiles were similar for spin-on (SOD) and chemical vapor deposited (CVD) films, even though the pore-size distribution and average pore size were different. Furthermore, profiles from dense CVD low-k films were also similar to those from porous films, even though the etch conditions were very different for the two cases. These results suggest porosity does not play a major role in F diffusion into SiCOH-based low-k materials. Profiles from the bottom of wide trenches were also similar to via-etched cases: high F concentration compared to non-etched regions, and penetration to 100nm below the trench bottom. The results of this study show F can be incorporated in low-k dielectric films during etch, and not completely removed during the subsequent resist strip. The F can interact with the strip chemistry to significantly etch the ultra-low-k material, and may cause reliability problems later.

4:40pm **PS1-MoA9 Effect of Species Density and Ion Scattering During Ashing on Ultra Low-@kappa@ Inter-Level Dielectric Films**, ***M.A. Worsley***[1], Stanford University*; S.F. Bent,* Stanford University, US*; N.C.M. Fuller, J. Doyle, M. Rothwell,* IBM TJ Watson Research Center*; T.L. Tai,* IBM Microelectronics Division*; T.J. Dalton,* IBM TJ Watson Research Center

The challenge of integrating ultra low-@kappa@ inter-level dielectric (ILD) materials in dual damascene integration schemes continues be a key issue in the microelectronics industry. For the 45 nm technology node and beyond, the ITRS roadmap predicts the need for porous organosilicate glass (OSG) materials. It has been shown that these porous OSG materials are even more susceptible to modification by photoresist ash plasmas than dense OSG films. Therefore, a more detailed understanding of the plasma characteristics that mitigate this modification is critical for successful integration of ultra low-@kappa@ ILDs in current integration schemes. Previous work by these authors has revealed several factors that influence modification using various techniques focused on analysis of the modified ILD. The present work combines that material analysis of the modified ILD with characterization of some key parameters in the plasma and at the plasma-surface interface. In this study, optical emission (OE) actinometry is used to measure the absolute densities of reactive radical species, and modeling of various plasma parameters (sheath thickness and positive ion mean free path) is used to estimate the significance of ion scattering in several ashing plasmas. Patterned structures in a porous OSG are ashed in conditions identical to that characterized and then analyzed using angle-resolved x-ray photoelectron spectroscopy (ARXPS). Data from the OE actinometry and modeling are combined with the ARXPS data to gain further insight into the mechanism by which modification of the OSG occurs in a patterned structure. Relevant results will be presented.

5:00pm **PS1-MoA10 Behaviors of Fluorocarbon Radical Temperature in Ar/N@sub 2@/C@sub 4@F@sub 8@ low-k Etching Plasma**, ***M. Nagai***, *M. Hori,* Nagoya University, Japan

Fluorocarbon plasma has been used for various fields of material processing. Recently, low dielectric (low-k) films are used for interlayer dielectrics in ULSI. The etchings of low-k films such as SiOCH have been developed with Ar/N@sub 2@/C@sub 4@F@sub 8@ plasma. One of the most serious problems of low-k films etching is a line edge roughness of resists, which is considered to be closely related with the behaviour of the radical. Recently, several techniques have been employed to measure fluorocarbon plasmas. Optical emission spectroscopy (OES) is a powerful tool to measure the radical temperatures because it does not require complicated system such as a laser. In this study, we investigated behaviors of radicals in 60 MHz capacitively coupled plasma (CCP) using Ar/N@sub 2@/C@sub 4@F@sub 8@ gases. OES was applied to measure rotational temperatures of CF radical and neutral molecule in the excited state. The N@sub 2@ rotational temperature was used for the neutral gas temperature in plasma. Infrared diode laser absorption spectroscopy (IRLAS) was applied to measure rotational temperatures and densities in the ground state. The CF rotational temperature was increased from 290 K to 430 K with increasing N@sub 2@ flow rate in Ar/N@sub 2@/C@sub 4@F@sub 8@ plasma. The rotational temperature using OES was equilibrium with the rotational temperature using IRLAS. It was found therefore that the rotational temperatures in the excited state were equilibrium with the rotational temperatures in the ground state. CF radical density was decreased from 1.5 x 10 @super 12@ cm@super -3@ to 0.6 x 10@super 12@ cm@super -3@, and F atom density was increased with increasing N@sub 2@ gas flow rate. The decrease of the CF radical density was due to the recombination with CF radical and N atom. One of the mechanisms of the increase of the CF rotational temperature was due to Franck-Condon effect with the increase of the electron temperature with N@sub 2@ addition.

Plasma Science and Technology

Room 304 - Session PS2-MoA

Silicon Etching

Moderator: D. Leonhardt, US Naval Research Laboratory

2:00pm **PS2-MoA1 Advanced Gate Stack Etch Modeling for 65 nm Node**, ***P.J. Stout***, *M. Shroff, T. Stephens, J.E. Vasek, O.O. Adetutu, S. Rauf, P. Ventzek,* Freescale Semiconductor, Inc.

A reactor/feature modeling approach has been applied to etching an advanced gate stack. The reactor model is HPEM (developed at the University of Illinois) and the feature model is Papaya (developed at Freescale). Papaya is a 2D/3D Monte Carlo based feature scale model. The reactor model supplies Papaya with the identity, flux rate, angular distribution, and energy distribution of specie incident on the feature surface. Papaya has also been coupled to lithography models to obtain the initial resist profile used as a mask during the etch process. The gate stack consists of polysilicon, an anti-reflective coating, and a hard mask. Discussed will be the 3D feature modeling of the plasma etch steps required to etch through the gate stack. The cummulative effect of the gate etch steps is studied. The influence each etch step has on subsequent steps will be explored. The photoresist profile and feature proximity effects on the final polysilicon profile will also be discussed.

2:20pm **PS2-MoA2 Investigation of Gate Oxide Behavior during Highly Selective Poly-Si Gate Etching for Triple Gate Transistors**, ***D. Kim***, *H.S. Lee, S.J. Park, Y.J. Jee, K.K. Chi, C.J. Kang, H.K. Cho, J.T. Moon,* Samsung Electronics, South Korea

Triple gate transistor, or FinFET, is one of the most promising candidates for the next CMOS technology. FinFETs have better capability for higher transistor current and better controllability for the short channel effect, especially for sub 50nm ULSI devices. However, focusing on the fabrication aspects, the structure of FinFET has difficulties to overcome, which are inherently originated from using the fin-shaped active structure: (1) The thin gate oxide should be able to stand for the large amount of gate poly-Si etching not to leave any residues on the sidewalls and the bottom area of

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[1] **PSTD Coburn-Winters Student Award Finalist**

the 3-dimensional fin structure. (2) We should also overcome the undercut or tapering of the gate profile on the top and sidewall of the active area, which also originate from the 3-dimensional fin structure. These directly affect transistor characteristics such as threshold voltage distribution. In this work, we report detailed analyses on highly selective poly-Si gate etching for a FinFET. Since poly-Si etching should be carried out to the bottom area of the fin with G-ox exposed to the etch environment, high etch selectivity to G-ox is required. From this point of view, we tried to fully figure out how initial G-ox is affected by polymer deposition on G-ox, etching of G-ox itself, and plasma oxidation of silicon beneath the G-ox, which compete with one another during the gate etching. Transmission Electron Microscope (TEM) analysis, G-ox wet etch rate measurement, and measurement of electrical characteristics such as density of interface trap, charge density, leakage current were implemented. Based on the above investigations, plasma oxidation is considered to play an important role in gate etching with thin G-ox. It is also shown that the silicon-containing byproduct during gate etching is indispensable for polymer generation.

2:40pm **PS2-MoA3 Silicon Etching Beyond the 90nm Technology Node: the Need for Total Parameter Flexibility***, **A.M. Paterson**, T. Panagopoulos, T.J. Kropewnicki, V. Todorow, A. Matyushkin, B. Hatcher, S. Pamarthy, N. Gani, A. Khan, S. Deshmukh, M. Shen, T. Lill, J.P. Holland,* Applied Materials **INVITED**

As CMOS technology node sizes push further into the nano-scale domain (sub 100nm) it has initiated new challenges for the silicon etching of logic and DRAM structures. In order to keep abreast of Moore's Law, new gate materials, geometries and architectures are currently being explored by IC manufactures with the intent of driving the node size to 32 nm by the end of this decade. Such device scaling brings new demands to wafer etch suppliers, with even more stringent etch requirements expected. At present, 90 nm technology is the smallest node in volume production, with the gate lengths being approximately 65 nm and CD bias requirements of 4 nm 3s over the entire 300 mm wafer, 3 mm edge exclusion. CD bias control is of paramount importance as it directly correlates to processor speed and cost. For smaller nodes the combination of resist trimming and curing (to prevent Line Edge Roughness (LER)) and process parameter flexibility become even more crucial in controlling the gate CD bias. This presentation will focus on the research and development work undertaken at Applied Materials to produce novel silicon etch equipment that will enable IC manufactures to obtain their goals for continued node size reduction. Experimental and theoretical work will be discussed showing the many novel features of an advanced 300 mm Applied Centura® DPS® process chamber for sub-65 nm gate, Shallow Trench Isolation (STI) and capacitor etches. This chamber has been designed to produce precise resist trimming / curing with total process step parameter flexibility allowing CD bias control of less than 3 nm 3s, 2 mm edge exclusion, for sub-65 nm technologies.

3:20pm **PS2-MoA5 Silicon Gate Etching using Amorphous Carbon Hard Mask***, **F. Lazzarino,*** CNRS/LTM, France*; P. Gouraud,* STMicroelectronics, France*; T. Chevolleau, B. Pelissier, G. Cunge, L. Vallier, O. Joubert,* CNRS/LTM, France*; T. Lill,* Applied Materials

Nowadays, the development of new integrated circuit generations requires the introduction of new materials. Among them, the amorphous carbon (a-C) is a promising candidate as a hard mask for gate etching processes due to its high selectivity to silicon (6:1). Moreover, since the conventional photolithography is not able to achieve resist linewidth lower than 80 nm, the trimming of a-C can be used as a new strategy to obtain sub-30 nm gate length. In this paper, an etch integration scheme using a-C hard mask is evaluated on 300 mm wafers and fully characterized for undoped, n-doped and p-doped wafers. The gate stack is composed of 1.2 nm SiON gate oxide, 100 nm polysilicon film, 100 nm PECVD amorphous carbon, 20 nm dielectric anti-reflective coating (DARC). The wafers are patterned with a 193 nm lithography and etched in an industrial inductively coupled plasma reactor. The resist trimming combined with the a-C trimming is investigated using different types of halogen chemistries containing oxygen (HBr/O@sub 2@, Cl@sub 2@/O@sub 2@,...) which allow to obtain sub-30 nm gate structures. The polysilicon gate is etched in conventional HBr/Cl@sub 2@/O@sub 2@ chemistries and the impact of the plasma parameters on the etch rates and both undoped and doped (n and p) gate profile is evaluated. Futhermore, chemical topography analyses by quasi in-situ X-ray Photoelectron Spectroscopy (XPS) are performed in order to correlate the etch profiles with the chemical composition of the passivation layers deposited on the sidewalls of the polysilicon gate.

3:40pm **PS2-MoA6 Atomic Scale Etching of Poly-Si in Inductively Coupled Ar and He Plasmas***, J.-H. Min,* Seoul National University, Korea*; S.H. Moon,* Seoul National University, Korea, South Korea*; Y.W. Kim,* FOI Korea Corporation, Korea*; C.B. Shin, **C.-K. Kim,*** Ajou University, Korea

For fabrication of novel Si-based devices, device structures with a high aspect ratio are increasingly required. The reactive ion etching is widely used for defining fine features, but energetic ions generated in a plasma are known to cause serious radiation damages. In a low-energy ion system, isotropic chemical reactions caused by neutrals become predominant and the deterioration of the pattern definition will occur. Therefore, a new concept of directional etching with minimum reaction energy is needed. In this work, atomic scale etching of poly-Si was performed by using a cyclic process of etchant adsorption and ion beam irradiation. This process is the same as the so-called atomic layer etching of single crystalline Si. Cl@sub 2@ was used as an etchant gas, and Ar or He ions generated in an inductively coupled plasma was used as an ion beam. The self-limiting characteristic of the etch rate with respect to the duration of ion irradiation for poly-Si etching was significantly different from that for single crystalline Si etching. That is, as the duration of the ion irradiation increased, the poly-Si etch rate was initially increased and converged to about 0.6Å/cycle and then rapidly increased, eventually showing a characteristic S curve. When He ions were used as an ion beam, the bias voltage region where the etch rates were smaller than the sputtering rates was observed, which was in contrast to the case where Ar ions were used as an ion beam. It is believed that this is because the size and mass of He ions are much smaller than those of chlorine atoms adsorbed on the poly-Si surface and therefore the chlorine atoms effectively prevent the poly-Si layer from being sputtered by the He ions.

4:00pm **PS2-MoA7 Spectroscopic and Real-Time Study of Ar@sup +@ and XeF@sub 2@ Etching of Si(100) by Second Harmonic Generation***, **A.A.E. Stevens**[1], P.M. Gevers, J.J.H. Gielis, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

To gain new insights into the fundamental processes occurring at surfaces during plasma etching, Second Harmonic Generation (SHG) has been employed to study the etching of Si(100) in an Ar@sup +@/XeF@sub 2@ beam etching experiment. SHG by a medium is only allowed when inversion symmetry of the medium is broken and is therefore possibly extremely sensitive to surfaces and interfaces. Using a Ti:Sapphire laser in the 710 to 920 nm wavelength range the strain-induced resonance of Si-Si bonds (2.70-3.44 eV) has been probed before, during and after etching by Ar@sup +@ ions and XeF@sub 2@. Low-energy (20-2000 eV) ions impinging onto the Si(100) create a damaged, amorphized Si layer, which leads to an enormous increase in the SH signal within less than 1 ML Ar@sup +@ dose, and broadening of the resonance, indicative for an amorphous medium. XeF@sub 2@ passivation of the surface after the ions are switched off reveals that the signal originates not only from the surface but also from a buried interface between the damaged and crystalline silicon. At the switch-on of the XeF@sub 2@ after the ion bombardment an immediate increase of the SH signal (at 3.42 eV) can be observed showing an instant reaction of F with the highly reactive amorphous silicon surface. For XeF@sub 2@ etching of Si(100) two separate spectral features in the SH signal can be distinguished. After the XeF@sub 2@ is switched off, the spectral features change, indicating a reconstruction of the reaction layer. Furthermore, dosing a hydrogen terminated surface with XeF@sub 2@ shows an increase in the SH signal over the full spectral range before the actual etching begins as a result of the initial binding of F to Si. These and other observations will be discussed, which have led to some surprising new insights in the etch mechanism of Ar@sup +@ and XeF@sub 2@ of Si(100), showing that SHG is a promising, powerful diagnostic tool for surface sensitive studies of etch mechanisms.

4:20pm **PS2-MoA8 Optimization of Cryogenic Processes with Plasma Diagnostics***, **T. Tillocher**, R. Dussart, X. Mellhaoui, P. Lefaucheux, N. Mekkakia Maaza,* GREMI - Université d'Orléans, France*; M. Boufnichel,* ST Microlectronics*; L.J. Overzet,* University of Texas at Dallas*; P. Ranson,* GREMI - Université d'Orléans, France

The so-called cryogenic process is a good alternative to the Bosch process for the etching of high aspect ratio structures. Indeed, etching and passivation occur simultaneously and anisotropic profiles result from a balance between these two mechanisms. Consequently, high etch rates can be reached with relatively smooth profiles. This equilibrium is put into

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[1] **PSTD Coburn-Winters Student Award Finalist**

evidence with mass spectrometry and optical spectroscopy on maskless silicon wafers : an oxidation threshold appears from one oxygen percentage in the SF@sub 6@/O@sub 2@ plasma where the etch rate drops. In such a case an overpassivation regime is reached, which strongly reduces the etching. We have shown that this threshold depends on the substrate temperature, the source power and the chuck self-bias : a lower temperature involves a higher sticking coefficient of oxygen on silicon and a higher energy transmitted to the wafer by the ions can prevent the formation of the layer. We think that these results, which can be characterized with a simple model, can also be correlated to the etching of high aspect ratio patterns. Indeed, the interaction between the surface and the radicals is quite similar on a bulk silicon wafer and on the sidewalls of the patterns. This appears to be a way to find the optimum oxygen flow. Plasma diagnostics, such as mass spectrometry, optical emission spectroscopy and Langmuir probe can also be used to optimize the other plasma parameters, especially the SF@sub 6@ flow and the source power. Finally, we will present performances which can be reached with optimized processes in the case of holes etching for the drilling of 400 µm thick silicon wafers.

4:40pm **PS2-MoA9 The Role of the Reaction Products in the Silicon Etching Cryogenic Process***, **R. Dussart**, X. Mellhaoui,* GREMI - Universit@aa e@ d'Orleans, France*; T. Tillocher,* GREMI, France*; P. Lefaucheux, N. Mekkakia Maaza,* GREMI - Universit@aa e@ d'Orleans, France*; M. Boufnichel,* ST Microelectronics, France*; L.J. Overzet,* Univ. of Texas at Dallas*; P. Ranson,* GREMI - Universit@aa e@ d'Orleans, France

The cryogenic process of silicon deep etching can be used in MEMS and power microelectronic component fabrication. In this process, a SF6/O2 plasma is used to etch high aspect ratio silicon microstructures. The bottom of the structure, which is submitted to ion bombardment, is etched while lateral etching is inhibited by the formation of a SiOxFy passivation layer. This layer, which only appears at low temperature and with oxygen, is continuously deposited on the microstructure sidewalls during the etching process. The formation of this passivation layer is not well characterized. It mostly desorbs when the wafer is warmed up to ambient temperature. In particular, the role of SiF4 (the main etching product) is not well understood. Experiments with SiF4/O2 and SF6/O2 plasmas were carried out to investigate the formation of the passivation layer. Mass spectrometry, profile characterization by SEM and ellipsometry measurements were carried out to better understand the role of SiF4 in the passivation layer formation in the cryogenic process.

5:00pm **PS2-MoA10 The Characterization of Silicon Trench Etching in a High Density Reactor Using Self-Excited Electron Resonance Spectroscopy (SEERS)***, **F.C. Session,*** Fairchid Semiconductor, US

The development and characterization of a medium depth Si trench process for power IC applications, was performed utilizing Self-Excited Electron Resonance Spectroscopy (SEERS). SEERS provides volume averaged plasma parameters such as electron collision frequency, electron density and sheath width by monitoring the non-linearity of the space charge sheath at the electrode. Several etch chemistries were investigated including SF@sub 6@/ O@sub 2@, Cl@sub 2@/ O@sub 2@, HBr/ O@sub 2@, HBr/SF@sub 6@/O@sub 2@ and Cl@sub 2@/SF@sub 6@/O@sub 2@ and their effect on etch rate and sidewall profile. Pressure appears to be the overwhelming parameter in terms of profile and has a large effect on the electron collision rate and electron heating mechanisms. The study of pressure effects on electron temperatures and electron collision rates have been performed@footnote 1@ but these parameters have yet to be correlated to the actual etch performance and trench morphology. This study looks at these relationships and their effects on the optimized trench process.

Plasma Science and Technology
Room Exhibit Hall C&D - Session PS-MoP
Plasma Science and Technology Poster Session

PS-MoP1 Minimum Area Required for Poly Etch Endpoint Detection*, R.L. Hill*, National Semiconductor

There have been somewhat arbitrary design rules implemented over the years dealing with how much open (non-resist covered) area is required on a product layout at a given layer to ensure robust endpoint detection. Design rules have been used at the typical layers that employ endpoint detection, e.g. poly, isolation, metal, capacitor. A systematic study of the poly layer endpoint detection is discussed in this report. A photolithographic method is introduced to measure the open area required for endpoint detection. Two etchers are studied: Lam 4400 poly etcher and a higher plasma density Lam TCP 9400SE. The endpoint signal versus percent open area and etch rate versus percent open area are presented. The minimum reticle open area required for the Lam 4400 endpoint detection was determined to be 25% and for the Lam 9400 it was 30%. Neither etcher showed an etch rate dependence on the percent open area.

PS-MoP2 Optical Second Harmonic Generation during Ar@sup +@ Etching of Silicon*, P.M. Gevers*, *A.A.E. Stevens, J.J.H. Gielis, H.C.W. Beijerinck, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Plasma etching of crystalline silicon can create a damaged layer in the top region of the silicon due to ion bombardment. Defects like strained and dangling silicon bonds are expected to be abundant in this region. The surface and interface sensitive nonlinear optical technique of second harmonic generation (SHG) is known to probe these defects in crystalline silicon and is therefore applied to study the plasma etching process. To circumvent the complexity of the plasma, the experiments are performed in a UHV multiple-beam setup, containing an ion source producing Ar@sup +@ ions with energies ranging from 20 eV to 2.5 keV. The data presented here will discuss the SH-signal in the photon energy range of 2.70-3.44 eV probing the strain-induced resonance. The silicon SH-signal exhibits an enormous increase when subjected to Ar@sup +@ ions. Careful analysis has localized the origin of the signal to both the surface of the silicon and the interface between the damaged and crystalline silicon. Future application of this diagnostic in the ion induced etching process promises to aid in the understanding of the etching process and might supply the possibility of monitoring the defects induced during processing.

PS-MoP3 The Study of Atomic Layer Etching Mechanism for Si with Various Substrate Orientations*, S.D. Park*, *C.K. Oh, M.S. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea

Atomic layer etching (ALET) can be an indispensable method in the fabrication of future devices such as nano-scale devices, quantum devices etc., because current etch technology utilizing reactive ion etching dose not have precise etch rate controllability and tends to damage the surface of the devices physically and electrically due to the use of energetic reactive ions to achieve vertical etch profiles. Generally, ALET of Si is composed of a cyclic process consisted of 4 steps; (1) adsorption of Cl@sub2@ on the Si surface, (2) evacuation, (3) Ar@super+@ ion beam irradiation to the substrate surface for desorption, (4) evacuation of the etch products. But, if Ar@super+@ ion beam is used for the desorption, the etched substrate can be charge damaged due to the charged particles such as positive ions and photons generated in the plasma. In this study, the ALET of Si was carried out for the first time using an Ar neutral beam instead of the Ar@super+@ ion beam to avoid charge-related damage during the desorption of halide and its ALET characteristics of Si by Cl@sub2@ were investigated. Especially, the ALET of Si having different orientations were investigated to understand the silicon etch rate per cycle.

PS-MoP4 The Effect of Oxide Thickness on Photoemission and Photoconduction Currents during VUV Irradiation*, J.L. Lauer*, *J.L. Shohet, G.S. Upadhyaya,* University of Wisconsin-Madison

Vacuum ultraviolet (VUV) radiation with photons in the energy range of 5 to 20 eV produced by high-density plasmas in plasma-processing systems can cause degradation to devices by changing the optical, mechanical, chemical and electrical properties of dielectrics. This is particularly important for thin films used in intermetal dielectric layers, because VUV is absorbed by the dielectric layer. Radiation charging of Si wafers coated with SiO@sub 2@ of different thicknesses in the range of 3000Å to 200Å was made by exposing them to synchrotron VUV radiation with photon fluxes in the range of 10@super 10@ -10@super 11@ photons/sec cm@super -2@ and photon energies of 7, 10, and 13 eV. The photoemission current and the current drawn by the substrate were monitored during each exposure. The tunneling and/or photoconduction current drawn through the oxide layer can be found by subtracting the photoemission current from the current drawn by the substrate. The total charge induced on the dielectric during VUV exposure consists of charge due to photoemission and electron-hole-pair creation, the net amount of which can be measured with a Kelvin Probe. The tunneling current (electrons injected from the silicon substrate into the oxide layer) causes a decrease in the charge produced by photoemission and electron-hole-pair creation. For most dielectrics, the threshold photon energy for photoemission is higher than that for electron-hole-pair production. The photoemission current can be minimized while the tunneling/photoconduction current increases, if the photon energies are below the threshold energy for photoemission but larger then the bandgap energy. VUV-exposed SiO@sub 2@ of various thicknesses shows the photon penetration depth as a function of energy and allows a quantitative description of the mechanisms that are involved in the photoconduction/tunneling processes taking place. @FootnoteText@ Work supported by NSF under Grants DMR-0306582.and DMR-0084402. .

PS-MoP5 Reduction of Gate Oxide Plasma Induced Damage via Silicon Nitride Backside Film*, H. McCulloh*, *C. Bossie, P. Allard, J. Garmon, C. Printy,* National Semiconductor

Plasma charging damage continues to be an issue in advanced semiconductor processing. In this work, the effect of residual films on the backside of the wafer on plasma damage induced at interconnect layers is investigated. Our experimental results show that intermetal dielectrics formed using fluorinated high density plasma (FHDP) are particularly prone to causing plasma induced damage (PID). The current work shows that residual material on the backside of the wafer has a strong impact on this damage. It is proposed that the presence of a conductive or semi-conductive backside film contributes to PID via electrical coupling through the electrostatic chuck (ESC) during the FHDP deposition process. Our results show that the presence of a uniform silicon nitride film on the back of the wafer dramatically reduces gate oxide damage caused by PID. Different backside film integration schemes were studied. PID was evaluated using metal antenna style test structures, with FHDP being deposited directly on the antenna.

PS-MoP7 Study of the Plasma-Induced Damage by Inductively Coupled Plasma in Pb(Zr,Ti)O@sub 3@ for FeRAM(Ferroelectric Random Acess Memory) Devices*, H.Y. Ko*, *K.R. Byun, Y.J. Jung, D.H. Im, D.C. Yoo, S.H. Joo, J.H. Ham, S.H. Park, H.S. Kim, K.K. Chi, C.J. Kang, H.K. Cho, U.I. Jung, J.T. Moon,* Samsung Electronics, South Korea

FeRAM is a non-volatile memory device based on the remnant polarization of ferroelectric film such as Pb(Zr,Ti)O@sub 3@ (PZT). The electrical properties of PZT films have proven to be excellent enough to apply to high-density FeRAM with 1T1C cell structure, in terms of the high remnant polarization and low crystallization temperature. However, it is known that high-density integration gives rise to several problems such as plasma-induced damage of PZT surface and surface composition change, which degrade FeRAM capacitor performances during the patterning of capacitor module. In this article, we carried out the investigations of the plasma-induced etching damage for the PZT thin films etched with the various gases chemistries (O2, Ar, BCl@sub 3@, Cl@sub 2@, CF@sub 4@, and mixture gases) on the microstructural and electrical properties. We analyzed the effect of individual and mixture gases on the near surface chemistry of the PZT thin films by XPS(X-ray Photoelectron Spectroscopy). We also used TEM(Transmission Electron Microscopy) and AFM(Atomic Force Microscope) for the structural and compositional change and roughness in the film through patterning of the real FeRAM devices. Finally, we evaluated the electrical properties (2Pr, fatigue, leakage current, retention) of the plasma-exposed PZT films through patterning of the real FeRAM devices.

PS-MoP8 Effective Stripping of Heavily Implanted Photoresist by Insitu-Bake Process*, S.-K. Yang,* Inha University, Korea*; J. Yang,* PSK Inc.*;* ***S.G. Park***, Inha University, Korea, Korea, Republic of

Popping of heavily implanted photoresist during plasma stripping, which is the main source of particulate contamination, occurs during the conventional stripping process using oxygen radicals at the temperature range of 250°C or higher. We introduce in-situ bake process (ISBP) prior to oxygen plasma stripping which does not suffer from low ashing rate or substrate damage. It is found that baking wafers at 250°C in the atmospheric pressure before evacuating the process chamber accelerates outgassing from bulk of photoresist without popping. Since heat transfer from heating wafer stage to wafer is better in air than that in vacuum, the stripping rate is also increased 50% because time to reach the process temperature is reduced. In this paper, we show the evidence of no-popping during bake-in-air step and the surface modification by bake-in-air by XPS analysis of carbon bonding. XPS data shows that baking in vacuum enhances more amorphous carbons in the photoresist surface than baking in air.

PS-MoP9 Plasma Etching of High-k and Metal Gate Materials in High-Density Chlorine-Containing Plasmas*, **K. Nakamura**, T. Kitagawa, K. Osari, K. Takahashi, K. Ono,* Kyoto University, Japan

As ultra large scale integrated circuit dimensions continue to be scaled down, high dielectric constant (high-k) materials such as HfO@sub 2@, ZrO@sub 2@, Al@sub 2@O@sub 3@, etc. are being required as gate dielectric to maintain the gate capacitance in smaller size. Moreover, for a gate stack with high-k dielectrics, gate electrodes of conventional polycrystalline silicon (poly-Si) tend to cause some problems of the depletion layer present in doped poly-Si gate materials, thus being replaced by metal electrodes such as Pt, Ru, TaN, TiN etc. For the fabrication of high-k gate stacks, an understanding the etching characteristics and mechanisms is indispensable for high-k dielectrics as well as metal electrodes. However, only a few studies have recently been concerned with their etching for the application to high-k gate stacks. In this study, we have investigated the etching of high-k materials of HfO@sub 2@ and metal electrode materials of Pt and TaN using high-density chlorine-containing plasmas excited by electron cyclotron resonance. The etching of HfO@sub 2@ etching was performed in BCl@sub 3@ plasmas at around 10 mTorr without rf biasing, giving a high etch selectivity (>>1) over Si and SiO@sub 2@ was obtained. At lower pressures, some deposition was found to occur on all material surfaces. The etching of Pt was performed in Ar/O@sub 2@ plasmas with high rf biasing, where highly selective Pt etching was achieved over HfO@sub 2@, Si, and SiO@sub 2@ by adding O@sub 2@ to Ar. Moreover, the etching of TaN was performed in Ar/Cl@sub 2@ plasmas, where high etch rates and high etch selectivity of TaN over HfO@sub 2@, Si and SiO@sub 2@ were obtained with low rf biasing. The etched profiles of Pt and TaN were also investigated; the etched profile of Pt was positive tapered, while the profile of TaN was found to be almost anisotropic. This work was supported by NEDO/MIRAI project and by Taiyo Nippon Sanso Corp.

PS-MoP10 Effects of Non-Volatility of Etch Products on Surface Roughness during Etching of Advanced Gate Stack Materials*, **W.S. Hwang**,* National University of Singapore*; W.J. Yoo,* National University of Singapore, singapore

As device dimensions continue to shrink, it becomes very crucial to understand evolution of surface roughness of device structures during etching. Until now, the mechanism on roughness evolution of Si surface from which volatile etch products are generated has been studied by various researchers. However, surface properties of new conducting materials such as TaN, TiN, HfN, and IrO@sub 2@ have rarely reported, although several reports on etching properties of advanced gate electrodes have been reported. In this work, we investigate the effects of the plasma parameters of ion energy (E), ion current density (J@sub i@) and ratio of ion flux over neutral flux (J@super +@ / J@sub n@) on the evolution of surface properties of these materials during etching. Etch rates of all samples are seen to obey the following empirical relation of ER(t)=C@sub 1@ E J@sub i@ (J@super +@/J@sub n@) (t) where ER is etch rate. The same approach was made to understand the evolution of surface roughness. It was found that surface roughness and etch rate are inversely related each other when volatile byproducts are formed, as shown in the following relation of @sigma@(t)=C@sub 2@ 1/E 1/J@sub i@ (J@sub n@ / J@super +@) t where @sigma@ is roughness value, in that surface roughness is proportional to pressure but inversely proportional to bias voltage. This relation implies that anisotropic profile can be attained without sacrificing the surface roughness. On the other hand, it is found that surface roughness and etch rate are proportional each other when non-volatile byproducts are formed, as expressed in the relation of @sigma@(t)=C@sub 3@ E J@sub i@ (J@super +@ / J@sub n@) t. That is, the formation of nonvolatile residues promotes surface roughening during ion induced chemical etching. In addition, results show that the average lateral distance between peak to peak increases with increasing surface roughness due to the redeposition and agglomeration of nonvolatile byproducts.

PS-MoP11 Highly Selective W/WN/Poly-Si Etching by using RLSA Microwave Plasma Source*, **T. Nishizuka**, K. Song Yun, K. Ishibashi, T. Nozawa,* Tokyo Electron, LTD., Japan*; T. Goto, T. Ohmi,* Tohoku Univ., Japan

W/WN/Poly-Si stack is used as a gate material of DRAM. For the etching of W/WN layer, high density plasma sources, such as ECR, ICP, etc., are usually applied with Cl@sub2@+O@sub 2@ gases.@footnote 1@ An important requirement of this etching is selectivity to Poly-Si. The selectivity can be improved by increasing oxygen fraction. However, actual selectivity used to be 1 or so because oversupply of oxygen causes deposition which is attributed to oxidized etching by-products, WO@sub 3@. In this study, we developed a RLSA (Radial Line Slot Antenna) microwave plasma source, and evaluated it on the W etching process. It can generate uniform surface-wave plasma with low electron temperature without magnets,@footnote 2,3@ and therefore it has compact chamber which reduces gas residence time. As for gas chemistry, N@sub 2@ addition was evaluated along with Cl@sub 2@+O@sub 2@ gases condition. As a result, we obtained high selectivity>5, W etch rate>100nm/min and straight W profile under the condition of fairly low stage temperature=60°C. We also found N@sub 2@ gas addition in high flow rate was effective to achieve both high selectivity and good profile. The role of nitrogen appeared to contribute to variety of radicals in the plasma rather than nitridation of Poly-Si and W surface. It probably controls the amount of reactive Cl and O radicals then reduces oxidization of by-products and Poly-Si etching rate. Furthermore, no charge-up damage has been observed on antenna MOS structure under any conditions. We believe that the high density plasma with low electron temperature and short residence time of gases lead to those performances. @FootnoteText@ @footnote 1@ T. Umezawa et.al., 1998 Dry Process Symposium, p49.@footnote 2@ H. Kokura et.al., 1999 Dry Process Symposium, p209.@footnote 3@ T. Ohmi, Semiconductor Manufacturing, Nov.2003, p110.

PS-MoP12 Extremely Thin Silicon Oxide Formation Using Pulse-Time-Modulated Oxygen Neutral Beam*, **C. Taguchi**, S. Fukuda, S. Noda, S. Samukawa,* Tohoku University, Japan

For next generation ULSI devices, high-k gate dielectric film is promising candidate since it provides both low gate-leakage and minimal electrical thickness in inversion. It is also important to form ultra-thin SiO@sub 2@ film between high-k film and Si substrate to avoid forming silicate. To minimize EOT of gate dielectric films, sub-1 nm fine thin SiO@sub 2@ film formation is indispensable. However, it is much difficult for conventional thermal-oxidation-processes to realize the requirement. To break through the problem, we proposed pulse-time-modulated neutral beam oxidation. In this new method, low energy (less than 10 eV) O@sub 2@ neutral beam radiation was modulated to the silicon substrate at the time constant of a few tens of µ seconds. That is, the oxidation process was modulated on the silicon surface. We first found that the SiO@sub 2@ thickness could be precisely controlled by changing the beam-on time in the pulse-time-modulated O@sub 2@ neutral beams without any radiation damages. It is speculated that the injected O@sub 2@ was diffused at a time constant of a few tens of µ seconds in the silicon. As a result, extremely thin SiO@sub 2@ film of less than 1 nm (minimum thickness:0.5 nm) could be formed on the silicon substrate by using the pulsed O@sub 2@ neutral beams. Our newly developed method is promising candidate to replace the thermal-oxidation-processes.

PS-MoP14 A Comparative Study on Dry Etching of TaN/HfO@sub 2@ Gate Stack Structure in Inductively Coupled Plasmas using Cl@sub 2@, BCl@sub 3@, and HBr Chemistries*, **M.H. Shin**, M.S. Park, N.-E. Lee,* Sungkyunkwan University, Korea*; J.Y. Kim,* Kookmin University, Korea, Rep. of Korea

Development of advanced high-k gate dielectrics and its integration into advanced nano-scale CMOS devices below 50-nm technology node has gained considerable attention recently because of the need for the replacement of ultrathin SiO@sub 2@ or nitrided SiO@sub 2@ gate dielectrics. For the integration of the high-k gate dielectric materials in the nano-scale CMOS devices, metal gate electrodes are expected to be used in the future. Currently, the metal gate electrode materials including TaN, TiN, HfN, WN, TaSiN and metal silicides are being widely studied for next generation devices with high-k gate dielectrics. 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 critical steps in the process integration of the front-end of the line (FEOL). In this work, as a model system for studying the etching characteristics of the metal gate electrode/high-k dielectric stack structures and etch rate selectivity of the metal gate electrode over the high-k dielectric layer, TaN/HfO@sub 2@ gate structure, was chosen. ICP etching characteristics of TaN(150nm)/HfO@sub 2@(80nm) gate stack structures on Si substrate were investigated by varying the process parameters such as etch gas mixing ratios (Cl@sub 2@/Ar/O@sub 2@, BCl@sub 3@/Ar/O@sub 2@, and HBr/Ar/O@sub 2@), the top electrode power, the DC self-bias voltage (V@sub dc@), and working pressure in an ICP etcher. To understand the role of etch gas chemistry in ICP etching, the relative change in the densities of ion radical and chemical binding states of etched TaN and HfO@sub 2@ surfaces were measured by optical spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS), respectively. The results of the etch rate and etch selectivity of SiO@sub 2@ to HfO@sub 2@ measured as a function of the various process parameters will be discussed in detail in conjunction with the OES and XPS analysis data.

PS-MoP15 Etching of Titanium Nitride*, D. Wu, B. Ji, E.J. Karwacki,* Air Products and Chemicals, Inc.

Titanium nitride (TiN) has many emerging new applications within semiconductor industry. It is being employed as a diffusion barrier in contacts, vias, trenches, and interconnect stacks, as well as an electrode material. The film is typically deposited by way of a batch CVD technique within a quartz tube furnace at a temperature lower than 150ºC. A cleaning method that removes TiN deposits from the inner surfaces of the deposition chamber, but does not damage the furnace is urgently needed by the industry. In this paper we report on our efforts to develop an effective process for TiN deposition chamber cleaning. Using our lab reactor as a screening tool, a variety of reactive gases and process conditions has been screened. For example, we have tested a thermal process using NF3, Cl2, and 5%F2. In each case, a temperature of higher than 200ºC is needed to start the etching reaction. To reduce the required temperature, remote plasma is used together with the thermal process. The process using remote NF3 plasma etches TiN at a rate of 1000 nm/min with a TiN/SiO2 selectivity of 8 at 140ºC. Surface analysis is also conducted to understand the etching mechanism.

PS-MoP16 Etching of Narrow Porous SiOCH Trenches using a TiN Metallic Hard Mask*, **M. Darnon,*** CNRS LTM - France, France*; N. Posseme,* ST Microelectronics - France*; D. Eon,* UJF - France*; T. David,* CEA LETI - France*; T. Chevolleau,* CNRS LTM - France, France*; L. Vallier,* CNRS LTM - France*; O. Joubert,* CNRS LTM - France, France

In CMOS technology, most of the interlayer dielectric materials achieve low k values by introducing porosity in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. Trench or via patterns are transferred into porous SiOCH (p-SiOCH) using a dual hard mask strategy. This approach minimizes the porous low k degradation induced during ash plasma exposure. Different hard masks (metallic such as TiN or TaN and inorganic such as SiO@sub 2@ or SiC) are currently under investigation to pattern 65 nm trenches targeted for the 45 nm node. This work is dedicated to the analysis of the impact of a metallic hard mask used to pattern narrow porous SiOCH trenches etched in fluorocarbon based plasmas. The stack investigated is composed of 600 nm p-SiOCH, 40 nm SiO@sub 2@, 45 nm TiN and 100 nm photoresist (PR). The 200 mm wafers are patterned using direct ebeam lithography to achieve aggressive trenches dimensions down to 50 nm. After TiN opening and resist removal, the SiO@sub 2@ and p-SiOCH layers are etched in two different industrial etching chambers: either an inductive (ICP) or a capacitive (MERIE) plasma source. Chemical topography analyses by X Ray Photoelectron Spectroscopy (XPS) and ion mass spectroscopy show that the condensation of low volatile Ti based etch by-products on the trench sidewalls can generate severe profile distortions. The profile distortion is strongly minimized and even suppressed by increasing the wafer temperature from 20°C up to 60°C. The TiN hard mask consumption during the dielectric etch process can be reduced by using highly polymerizing chemistries which contributes to the formation of a fluorocarbon overlayer on top of the mask. The patterning of very narrow trenches reveals that one of the main issues is the faceting of TiN hard mask, leading to unacceptable profile distortions. The impact of the plasma parameters on the profile distortion of narrow trenches will be presented and discussed.

PS-MoP17 A Stacked Mask Process (S-MAP) for Precise CD Control using 100 MHz CCP RIE*, **H. Hayashi**, J. Abe, A. Kojima, I. Sakai, T. Ohiwa,* Toshiba Corporation, Japan

The stacked mask process (S-MAP)@footnote 1@ has been developed to provide improved critical dimension (CD) control in deep UV lithography, where it is necessary to use thin photo resist (P.R.) susceptible to etch erosion. In S-MAP, the P.R. pattern is first transferred to a spin-on-glass (SOG) layer, then to spun-on carbon film. An oxygen-based chemistry has been widely used for organic film etching. However, it tends to cause a bowed profile due to excess oxygen radicals. Therefore, a nitrogen-based chemistry is often used, where a straight profile can be obtained because of the sidewall protection effect by nitrogen. But, when the nitrogen-based chemistry was applied to the etching of stacked film structure such as S-MAP, the SOG film peeled at the interface of SOG and carbon films during etching under some conditions. The mechanism of SOG peeling in nitrogen-based chemistry was examined by analyses of the SOG/carbon stacked film after etching, and it was found that nitrogen gas was trapped in the stacked film. On the other hand, the SOG surface exposed to the plasma was densified by ion irradiation. It is assumed that, as etching progressed, nitrogen molecules gradually accumulated in the stacked film until the nitrogen gas pressure in the film became high enough to cause SOG peeling. By using the 100 MHz capacitive coupled plasma (CCP) which can realize low pressure and low ion energy simultaneously, carbon film etching using nitrogen-less gas chemistry without bowing was realized, by suppression of oxygen radical density at low pressure. Furthermore, selectivity to SOG improved because of the low ion energy, and CD loss due to SOG erosion was reduced. In conclusion, S-MAP for the 55 nm pattern size with precise CD control was realized by using 100 MHz CCP RIE using nitrogen-less gas chemistry. @FootnoteText@ @footnote 1@J. Abe et al., Symp. Dry Process, (2001) 187.

PS-MoP18 Characterization Methodologies for Unsaturated 1,3-C4F6 Plasma used to Investigate Aspect Ratio Dependent Etch and Etch Characteristics with Comparison to Saturated C-C4F8*, **T.L. Anglinmatumona,*** San Jose State University*; C.T. Gabriel,* Advanced Micro Devices*; E. Allen,* San Jose State University

The scaling of device features below 65 nm may encounter severe challenges such as the mass transport of CF2 and CF polymer precursors to the bottom of the feature due the generation of large molecular-weight radicals in saturated chemistries. As aspect ratios continue to increase due to the shrinking of the via hole diameter, saturated chemistries such as octafluorocyclobutane (c-C@sub 4@F@sub 8@) will no longer provide the etch performance required for ULSI. Hexafluorobutadiene (1,3-C@sub 4@F@sub 6@) is being proposed as an alternative gas to c-C@sub 4@F@sub 8@ for via etching in an inductively coupled plasma system. Profile slope, etch selectivity, CD bias and etch rates were investigated as a function of cathode temperature, rf bias power and chamber pressure. Optimum process conditions were identified based on a statistical design of experiment. Hexafluorobutadiene at optimized process conditions improved the etch parameters overall by 2X in comparison to c-C@sub 4@F@sub 8@. Aspect ratio dependent etching (ARDE) was reduced due to 1,3-C@sub 4@F@sub 6@ unsaturated bond configuration and improved process conditions.

PS-MoP20 Effects of N@sub 2@ Additive Gas on Etching Characteristics of Silicon Oxide Layers in F@sub 2@/N@sub 2@/Ar Remote Plasmas*, **J.Y. Hwang**, D.J. Kim,* Sungkyunkwan University, South Korea*; N.-E. Lee,* Sungkyunkwan University, South Korea, Korea*; C.Y. Jang, G.H. Bae,* ATTO, Korea

In this study, remote plasma etching characteristics of silicon oxide layers were investigated in F@sub 2@/Ar and F@sub 2@/N@sub 2@/Ar plasmas. A toroidal-type remote plasma source was used for the generation of remote plasmas. The effect of additive N@sub 2@ gas on the etch rates of various silicon oxide layers, including PE-oxide (deposited by PECVD using SiH@sub 4@ and N@sub 2@O), O@sub 3@-TEOS oxide (deposited by thermal CVD using ozone and TEOS precursor) and BPSG (borophosphosilicate glass), was investigated by varying the various process parameters, such as the additive gas N@sub 2@ flow rate and the substrate temperature. The species emitted during cleaning were monitored by Fourier transformed infrared spectroscopy (FT-IR) and residual gas analysis (RGA). The etching rate of the silicon oxide layers is increased 20~25% by adding N@sub 2@ gases to the optimized F@sub 2@/Ar chemistry. Under the current experimental conditions, the largest increase in the etch rate of the silicon oxide layers was observed at the flow condition of F@sub 2@:N@sub 2@=2:1. The etch rates of the silicon oxide layers were increased by the factors of 8.7, 8.3, and 35.7 for PE-oxide, O@sub 3@-TEOS oxide, and BPSG, respectively, at the conditions of F@sub 2@(1500 sccm)/N@sub 2@(750 sccm)/Ar (500 sccm) as the substrate temperature increases from 25 to 350°C. The additive N@sub 2@ flow rate and the substrate temperature were found to be the most critical parameters in determining the etch rate of the silicon oxide layers.

PS-MoP21 Comparison of C@sub 4@F@sub 6@ with C@sub 4@F@sub 8@ Chemistry for Deformation of ArF Photoresist and Silicon Dioxide Etching using Dual Frequency Superimposed (DFS) Capacitive Coupled Plasmas*, **C.H. Lee**, C.H. Park, N.-E. Lee,* Sungkyunkwan University, Korea

As the critical dimension (CD) of advanced CMOS devices is scaled down below 100 nm, 193 nm ArF photoresist (PR) needs to be used as a mask for various etching processes including silicon nitride (SiN) hard-mask opening. Recently, dielectric etch process using ArF photoresist mask by dual frequency superimposed (DFS) capacitive coupled plasma (CCP) has attracted a lot of attention. High frequency (HF) power is used to enhance plasma density and low frequency (LF) power is used to control ion bombardment to the wafer. During dielectrics etch process using DFS-CCP, understanding of ArF photoresist deformation is very important. It has been found that the most serious problems of the hard-mask open process with ArF PR are striation, wiggling, and agglomeration of the PR. In this study, we investigated deformation of ArF photoresists and silicon dioxide etching by varying the process parameters such as HF(13.56, 27.12, and 60 MHz)/LF(2 MHz) power ratio, O@sub 2@ flow, CH@sub 2@F@sub 2@ flow rate and etch chemistry (C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@/ CH@sub 2@F@sub 2@/ O@sub 2@/ Ar). Characterization of surface chemical change was performed by X-ray photoelectron spectroscopy (XPS). Surface morphological changes also investigated by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Also, morphological changes of surface and line edges in ArF PR, SiO@sub 2@ etch rate, selectivity over PR during etching of ArF PR/BARC/SiO@sub 2@ structures were investigated. Effects of process parameters on the etch results will be discussed in detail.

PS-MoP22 Influence of the Positive Ion Composition on the Ion-Assisted Chemical Etch Rate of SrTiO@sub 3@ Thin Films in Ar/SF@sub 6@ Plasmas*, O. Langlois, L. Stafford, **J. Margot**,* Universite de Montreal, Canada*; M. Gaidi, M. Chaker,* INRS-Energie, Materiaux et Telecommunications, Canada

The control of the etch rate is one of the critical issues related to the patterning of functional thin films relevant for applications in electronic, opto-electronic and optical integrated devices. This etch rate is known to be strongly influenced by the reactive neutral and total positive ion density, by the positive ion energy, and by the surface temperature. For plasmas sustained in molecular gases such as BCl@sub 3@, CF@sub 4@, C@sub 4@F@sub 8@, and SF@sub 6@, more than one positive ion species can be present simultaneously in the plasma. It is therefore likely that in addition to the previous parameters, the relative concentration of each positive ion species somewhat impacts the etch rate. In this work, we investigate the influence of the positive ion composition on the ion-assisted chemical etch rate of strontium-titanate-oxide (SrTiO@sub 3@) thin films in Ar/SF@sub 6@ plasmas, using a parametric approach. In this context, we characterize the influence of the operating parameters (e.g. gas pressure and absorbed power) on the positive ion density of each charged species by using plasma sampling mass spectrometry and Langmuir probes. It is found that as either the gas pressure increases or the absorbed power decreases, the relative concentration of molecular positive ion species such as SF@sub 3@@super +@ and SF@sub 5@@super +@ strongly increase. Based on these results, it is possible to define an effective positive ion mass M that describes the overall positive ion composition of the plasma. The SrTiO@sub 3@ etch yield Y (i.e. the number of atoms desorbed from the surface per incident ion) is shown to be a decreasing function of the effective ion mass M, in excellent agreement with the predictions of a simple ion-assisted chemical etching model.

PS-MoP23 In Situ Etching of (Pb,Sr)TiO@sub 3@ Thin Films by using Inductively Coupled Plasma*, **G.H. Kim**, K.T. Kim, C.I. Kim,* Chungang University, Korea

To overcome the limitations of conventional capacitor structure, high-k material, for example, (Ba,Sr)TiO@sub 3@ (BST) and (Pb,Sr)TiO@sub 3@ (PST), have been intensively studied for a number of integrated devices such as dynamic random access memories (DRAM) because high dielectric constant, lower crystallization temperature and low leakage current. However, BST thin film possesses a satisfactorily characteristics, it was known that a post heat treatment at a high temperature was essential to obtain good electrical property. The heat treatment at high temperature can cause deleterious effects on an electrode, barrier metal, and contact plug. On the other hand, PST thin film can be a promising material due to its high dielectric constant, paraelectricity at normal operating temperature and good electrical properties. In this study, inductively coupled plasma etching system was used for PST thin film etching. The chlorine base plasmas were characterized by optical emission spectroscopy (OES), Langmuir probe and quadrupole mass spectrometer (QMS) analysis. OES and QMS were used for the analysis of byproduct.

PS-MoP24 Surface Etching Mechanism of Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ Thin Films using Quadrupole Mass Spectroscopy and X-ray Photoelectron Spectroscopy*, **J.G. Kim**, G.H. Kim, K.T. Kim, C.I. Kim,* Chungang University, Korea

Ferroelectric thin films are employed for ferroelectric random access memories (FeRAMs). FeRAMs offer non-volatility, a lower voltage operation and larger write cycle numbers. (Bi@sub 4-x@La@sub x@)Ti@sub 3@O@sub 12@ (BLT) thin films was proposed as a promising ferroelectric material that does not exhibit the polarization fatigue, does have bigger remanent polarization value than that of SrBi@sub 2@Ta@sub 2@O@sub 9@. Accordingly, for high density FeRAMs, the etching mechanism of BLT thin films must be understood by investigation of both chemical and physical reactions between plasma species and BLT thin films. In this paper, the etching properties of BLT thin films in inductively coupled Ar/Cl@sub 2@ plasma was investigated with various gas mixing ratio. For investigation of chemical reaction with ions and radicals, in-situ monitoring using quadrupole mass spectroscopy (QMS) with 250µm orifice was performed. After etching process, etched BLT thin film surface was analyzed with X-ray photoelectron spectroscopy (XPS), since etching byproducts of BLT thin films has non-volatile species and re-deposited its surface. One could explain how to react the ions and radicals on the surface of BLT thin films to combine the QMS scanning data and the analyzed data of XPS spectrum.

PS-MoP25 The Etching Characteristics of LaNiO@sub 3@ Thin Films in CF@sub 4@/Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/Ar Gas Chemistry*, G.H. Kim, K.T. Kim, **C.I. Kim**,* Chungang University, Korea*; D.P. Kim,* KDG Engineering Co., Ltd., Korea*; C.I. Lee,* Ansan College of Technology, Korea*; T.H. Kim,* Yeojoo Technical College, Korea

During the last decade, ferroelectric thin films have been attracting much attention for nonvolatile memory application. Among ferroelectric material, zirconate titanate (Pb(Zr,Ti)O@sub 3@ : PZT) thin films have been studied extensively because PZT has high dielectric constant and bistable polarization. Platinum (Pt) film usually employed as an electrode for metal-ferroelectric-metal (MFM) capacitor for 1 transistor-1 capacitor structure (1T/1C). However, Pt/PZT/Pt capacitors suffer from poor resistance on fatigue property due to generation oxygen vacancies in interface of Pt/PZT during exposing to a hydrogen environment. Therefore, metal-oxides (IrO@sub 2@ and RuO@sub 2@) have been studied for top electrode. However, IrO@sub 2@ and RuO@sub 2@ have the problems that metal-oxides are easily transferred to metallic Ir and Ru under vacuum and high temperature conditions, resulting in degradation of ferroelectric properties by H@sub 2@ diffusion. Recently, LaNiO@sub 3@ (LNO) electrodes are challenged as top and bottom electrodes. Because LNO has a pseudo cubic perovskite structure, the close lattice constant (3.84 Å) to PZT (4.04 Å) and a good metallic property. In order to realize highly integrated FRAMs, the etching process must be developed. In this case, the task of primary importance is to understand etching mechanism to open the ways for the optimization of etching process. Unfortunately, there is only one report for etching LNO thin film. Therefore, the etching mechanism of LNO films should be understood in terms of etching system and gas mixture. In this work, we investigated etching characteristics and mechanisms of LNO thin films using CF@sub 4@/Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/Ar mixtures in inductive coupled plasma (ICP) system. Plasma diagnostic was represented by quadrupole mass spectrometer and Langmuir probes measurements.

PS-MoP26 Low Damage Etching of III-V Semiconductors using a Low Angle Forward Reflected Neutral Beam*, **B.J. Park**, K.S. Min, H.C. Lee, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea

Plasma etching is essential in the fabrication of compound semiconductor devices due to the requirements of anisotropic profiles and submicron features for optoelectronic integrated circuits, microwave devices, lasers, etc. Any process-related damage such as electrical damage and surface modification remaining during the processing may cause serious problems due to the size limitation of the devices. Therefore, etch processes without or negligible damages are required. In this study, fluorine based directional neutral beams were formed by low angle reflection of the energetic directional fluorine-based reactive ion beams generated by a fluorine-based inductively coupled plasma (ICP) gun. GaAs and GaN were etched and their etch characteristics such as etch rates and etch damage due to the etching were investigated. As a comparison, GaAs and GaN were etched by a conventional ICP and their damage characteristics were compared. When dry etch damage of the etched GaAs and GaN were investigated using PL and PRS, no damage could be observed when the neutral beam etching was used while the GaAs and GaN etched by the ICP showed significant surface damage. No damage by the energetic neutral beam etching appears to be related to the insignificant reaction of the neutrals with the electrically active surface states during the etching.

Plasma Science and Technology
Room 302 - Session PS+BI-TuM

Plasmas in Bioscience

Moderator: P. Favia, University of Bari, IMIP-CNR, Plasma Solution Srl, Italy

8:20am **PS+BI-TuM1 Plasma Polymerisation of Ethanethiol***, **S.L. McArthur**, G. Mishra, A.G. Shard,* University of Sheffield, UK

The past years have seen significant development and use of functional polymer surfaces for bio-medical applications. Plasma polymerisation has proved to be one technique to generate functional surface in a single step process. Spontaneously reactive thiol surfaces produced by various wet chemistry routes have been extensively characterised as models to study surface-ligand interactions. This project aims to develop thiol functionalized surfaces utilizing plasma polymerisation of ethanethiol and with 1, 7 Octadiene as a diluent monomer. The deposited film properties were determined by X-Ray photoelectron spectroscopy and a fluorine marker was used to label any functional thiol groups present. It was observed that plasma polymerisation of ethanethiol at low discharge power resulted in a sulphur rich stable coatings and by increasing the power the coating resembled monomer composition in terms of atomic percentages, but none of the used conditions generated any detectable thiol groups. Mixing 1-7 Octadiene in a ratio of 1:1(v/v) in the gaseous feed resulted in an interesting change at high powers in the film properties with generation of 3-4% detectable active thiol groups without affecting the stability of the film. It is believed that the introduction of a diluent monomer at high powers has reduced the amount of available sulphur for crosslinking which dominates the deposition mechanism at low powers and has created a reaction pathway which favours the generation of thiol groups at the surfaces.

8:40am **PS+BI-TuM2 A Novel, Single-Step Method for the Preparation of Chemical Gradient Surfaces Using Non-Uniform Plasma-Deposition***, **T.R. Gengenbach**, P.G. Hartley, H. Thissen, K.M. McLean, L. Meagher, G. Johnson,* CSIRO Molecular Science, Australia

Gradient surfaces are characterised by a gradual and systematic variation of one or more chemical and physical properties along a specific direction. They are of increasing importance in combinatorial chemistry and materials science where they are being used to generate libraries of widely varying surface properties to study interfacial phenomena. In biomaterials research gradient surfaces can be employed to rapidly explore multi-variable parameter space, either to investigate how relevant variables (e.g. surface chemistry, wettability, charge) affect biocompatibility, or alternatively, to accelerate the optimisation of coupling strategies for covalent attachment of secondary layers. Radio frequency glow discharge plasma polymer coatings form robust thin films which contour and adhere strongly to the surfaces of polymeric and other materials. Their ability to modify surface properties, either by enhancing biocompatibility, or by introducing defined chemical functionalities at interfaces for the subsequent coupling of bioactive molecules, have seen their widespread application in the field of biomaterials research. We have developed a novel method to deposit plasma polymer coatings with systematically varying properties along the surface. In a standard plasma reactor with capacitively coupled electrodes the substrate to be coated is placed on a large flat horizontal base electrode (earthed); the second, specially shaped top electrode (active) is lowered to within millimetres of the substrate surface. The resulting plasma discharge is spatially non-uniform and produces surfaces with a strong gradient of chemical/physical properties. By controlling the shape of the top electrode we have also prepared patterned surfaces with well defined regions of widely different properties (e.g. density of specific functional groups). These gradient surfaces have been evaluated with respect to the biological response, such as protein adsorption and cell attachment.

9:00am **PS+BI-TuM3 Mechanistic Musings on Plasma-Enhanced CVD of Polymeric Materials***, **E.R. Fisher**,* Colorado State University **INVITED**

Plasma-enhanced chemical vapor deposition (PECVD) is a valuable technique for deposition of polymeric materials with wide ranging applications, including micropatterns for fabrication of multianalyte biosensors, diagnostic tests, DNA microchips, and genomic arrays. One ongoing issue with PECVD processes is controlling and tailoring the molecular level chemistry, both in the gas-phase and at the gas-surface interface such that predictable and reproducible film chemistries can be created. One method for controlling the overall deposition is to use pulsed, downstream or remote deposition processes. Moreover, understanding surface interactions of plasma species provides critical molecular level information about PECVD processes. The imaging of radicals interacting with surfaces (IRIS) technique examines interactions of radicals during plasma deposition using laser-induced fluorescence (LIF) to provide spatially-resolved 2D images of radical species involved in film formation. IRIS allows for direct determination of radical-surface interactions during plasma processing. IRIS data for species in plasma polymerization and plasma modification systems will be presented, along with addition film and gas-phase composition data. IRIS results that will be discussed include data on fluorocarbon radicals (CF and CF@sub 2@), main group hydrides (SiH, OH, NH, and CH), and nitrogen-containing molecules (NH, NH@sub 2@, CN) in relationship to various plasma polymerization systems of interest to the microelectronics and coating industries. Correlation of gas-phase data, surface analysis, and plasma-surface interface reactions will also be presented to provide more comprehensive mechanisms for overall plasma polymerization processes. Examples will also be provided from polymer film and fiber modification systems.

9:40am **PS+BI-TuM5 Application of Plasma Discharges in the Biomedical Field: Biological Decontamination and Sterilization of Surfaces***, **F. Rossi**,* European Commission-Joint Research Centre, Italy **INVITED**

Every year, thousands of patients die from nosocomial infections got in hospital after surgical intervention. Those infections are directly linked to bacterial contamination of medical devices surfaces that are used during operation. Moreover, interaction of specific biomolecules like phospholipids or lipopolysaccharides (LPS) or certain proteins with organisms can be a major cause of diseases. Prominent examples are pyrogenes - lipopolysacharides (LPS) and lipoteichoic acids (LTA) -, which cause fever in human body and are potentially lethal after contact with blood. In some cases the secondary or tertiary structure of proteins is responsible for their biological properties. Important example is PrP (prion) which becomes pathogenic after a change of its structure. The contaminated surface (e.g. medical devices, accessories, work surface or tissue) cannot be decontaminated with current sterilisation practices without inducing major damage to the substrate or tissue itself, because of the high temperature used, or chemical reaction with the surface. In the present work, the inactivation or modification of biologically potentially harmful molecules is addressed in a combined approach using low pressure plasma discharges with non toxic gas mixtures. The emerging species fluxes of these plasmas are measured. Different characteristic biomolecules (LPS, LTA, proteins etc. as well as whole micro-organism cells) are exposed to the plasmas and the changes induced are monitored in-situ using infrared spectroscopy as well as ex-situ using biochemical and structural analysis as a function of the gas mixture and plasma parameters. Different potential mechanisms (etching, UV radiation, chemical reactions) are presented. The gained knowledge on the interaction of plasma discharges with pathogenic biomolecules and microorganisms allows a targeted development of decontamination strategies for very resistant species. The potential applications are in the field of surface decontamination and sterilisation of medical objects and opens large possibilities of applications in the field of security.

10:20am **PS+BI-TuM7 Biological Response to Plasma Processed Materials**, ***L.C. Lopez**,* University of Bari, Italy*; R. Gristina,* CNR-IMIP Bari, Italy*; L. Detomaso, P. Favia, R. d'Agostino,* University of Bari, Italy **INVITED**

The demand of biomedical implants significantly increases every year and several approaches have been investigated to develop surfaces which are recognized by specific proteins of the biological milieu, ranging from template materials, to surfaces that mimic receptor sites, to biologically inspired materials. Other surface modifications approaches deal, instead, with the immobilization of biomolecules (heparine, carbohydrates, peptides, enzymes, etc.) on biomedical surfaces, to induce the growth of cells, to act as sensors in immunodiagnostics or to exhibit blood compatibility. Low temperature plasma modification processes represent an appealing tool, versatile and environmental friendly, to selectively modify materials to be used for medical devices. Surface properties of biomaterials (chemical, biological, tribological) can be selectively plasma driven to achieve specific biological response, leaving the bulk features unaltered.@footnote 1@ Furthermore, a promising strategy to control the interaction between biomaterials and biological environments, applies to binding of biomolecules to plasma modified polymers by a stable bond with surface functional groups (OH, COOH, NH@sub2@, etc.).@footnote 2@ RGD-containing peptides and galactose immobilization on plasma processed substrates, recently investigated in our group, clearly highlighted a strict correlation between specific cellular behaviour and immobilised molecules. These results plainly indicate that coupling plasma modification processes with precise biomolecules immobilization pathways may represent a successful approach to address biocompatibility and biorecognition requirements of biomaterials. @FootnoteText@ @footnote 1@ B.D. Ratner in: Plasma Processing of Polymers, R. d'Agostino, P. Favia, F. Fracassi ed., Kluwer Acad. Publ., NATO ASI Series, E: Appl. Sci., Vol. 346, 1997.@footnote 2@ L. C. Lopez, R. Gristina, G. Ceccone, F. Rossi, P. Favia, R. d'Agostino Surface and Coatings Technology, 2005, in press.

Plasma Science and Technology
Room 304 - Session PS-TuM

Plasma Surface Interactions I

Moderator: E.C. Benck, National Institute of Standards and Technology

8:20am **PS-TuM1 Investigation of Plasma-Surface Interaction by Sheath-Lens Focusing Effects*, E. Stamate,*** *H. Sugai,* Nagoya University, Japan

Present trends in nano-technologies involve reactive plasmas of complex chemistry that makes it difficult to evaluate and control all surface reactions. Recently we discovered that the sheath forming to a biased target interfacing an insulator acts as an electrostatic lens that exhibits two focusing effects.@footnote 1@ The discrete-focusing leaded to the formation of a passive surface of no charge impact, near the target edge, and the modal-focusing resulted in the formation of certain modal-spots and/or modal-lines on the active surface. So far, several applications to plasma diagnostics (negative ion detection, sheath thickness measurements) and ion flux control in plasma immersed ion implantation have been reported. In this work we are demonstrating by simulations and experiments the possibility to use the focusing effects to investigate the surface reactions induced by beams of focused positive and negative ions and/or dusty particles. Measurements are done in DC and ICP discharges using Ar/SF6, O2 and CF4 gases. Sheath accelerated ion beams with energy ranging from 50 to 500 eV are directed by focusing effect to samples of various geometries (disk, square and complex three-dimensional shapes) made of different materials (metals or semiconductors). Surface investigation by AFM and SEM shows the influence of the ion dose and incidence angle to the sputtered profile. Depending on the competition between sputtering and deposition of by products the formation of cluster like structures is also observed. Simulations of the sheath potential structure and ion and dust kinetics are done in three dimension. The ion and dust flux on target surface is found in an excellent agreement with experiments. This work was partialy supported by the 21st Century COE Program of MEXT, Japan. @FootnoteText@@footnote 1@ E. Stamate and H. Sugai, Phys. Rev. Lett. 94, 125004 (2005).

8:40am **PS-TuM2 Effects of Polymer Deposition on Density Stabilization and Loss Rate of Radical Species in Fluorocarbon Plasmas*, K. Kumagai,*** *K. Nakamura,* Chubu University, Japan*; K. Oshima, T. Tatsumi,* Sony, Japan

Fluorocarbon discharges have been widely used for etching processes of dielectric thin films for microfabrication. However, these have suffered from various problems, in particular, repeatability of the etching characteristics. The problem becomes recently severe due to narrow process margin for next generation ULSI devices. One of the major origins is plasma-surface interaction on polymer-deposited vessel wall, leading to significant time-variation of radical composition of the plasma. Alternating ion bombardment (AIB) method has been proposed to reduce such interactions by applying an RF bias to the chamber wall.@footnote 1@ We reports on the effects of polymer deposition on the density variation and loss rate of radical species in fluorocarbon plasma reactors. 13.56 MHz inductively-coupled plasmas were produced in Ar-diluted C@sub 4@F@sub 8@ gases in a stainless steel chamber in which two semi-cylindrical electrodes are set. A 400 kHz RF source serves alternating negative bias to the electrodes, and the AIB could control the deposition rate of the polymer on the biased wall. The radical density reached a steady state more quickly when the polymer deposition was suppressed with the AIB. In order to investigate the mechanism, as a parameter of thickness of the polymer, we measured a decay time of the radical density immediately after only the bias was turned off keeping the plasma-existing conditions. The delay time corresponding to a loss rate of the radical species increased with an increase in the polymer thickness, suggesting that the polymer deposition affected the loss rate. To keep the polymer thickness will be crucial for stabilization of the radical density. @FootnoteText@ @footnote 1@K. Nakamura et al: J. Vac. Sci. Techonol. A 18 (2000) 137.

9:00am **PS-TuM3 Angular Dependence of Si@sub 3@N@sub 4@ Etch Rates and the Etch Selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ at Different Bias Voltages in a High Density C@sub 4@F@sub 8@ Plasma*, J.-K. Lee,*** *J.-H. Min, S.H. Moon,* Seoul National University, South Korea

The dependence of Si@sub 3@N@sub 4@ etch rates and the etch selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ on the ion-incident angle was studied at different bias voltages in a high density C@sub 4@F@sub 8@ plasma. A Faraday cage and specially designed substrate holders were used to accurately control the angle of ions incident on the substrate surface. The normalized etch yield (NEY), defined as the etch yield normalized to one obtained on a horizontal surface, was unaffected by the bias voltage in Si@sub 3@N@sub 4@ etching but increased with the bias voltage in SiO@sub 2@ etching, in the range of -100 V ~ -300 V. The NEY changed characteristically, showing a maximum, with the ion-incident angle in the etching of both substrates. In Si@sub 3@N@sub 4@ etching, the maximum NEY of 1.7 was obtained at 70° in the above bias voltage range. However, the increase in the NEY with the ion-incident angle was smaller for SiO@sub 2@ than for Si@sub 3@N@sub 4@ and, consequently, the etch selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ decreased with the ion-incident angle. The etch selectivity decreased with the ion-incident angle to smaller extents at high bias voltages because the NEY of SiO@sub 2@ was high under this condition. To understand the characteristic changes in the NEY for different substrates, we estimated the thickness of a steady-state fluorocarbon (CF@sub x@) film formed on the substrates. The thickness of a film on Si@sub 3@N@sub 4@ changed with the ion-incident angle, showing a minimum at 70°, and the film thickness was reduced at high angles to smaller extents on SiO@sub 2@ than on Si@sub 3@N@sub 4@. These results indicate that the NEY can be correlated with the thickness of a steady-state CF@sub x@ film formed on the substrate surfaces.

9:20am **PS-TuM4 Fluorocarbon Film Deposition in a Gap Structure and Correlation With Trench Sidewall Angle for Fluorocarbon Chemistries in Capacitively Coupled Discharges*, L. Ling,*** *X. Hua, B. Orf, G.S. Oehrlein,* University of Maryland at College Park*; E.A. Hudson,* Lam Research Corp.*; P. Jiang,* Texas Instruments*; Y. Wang,* National Institute of Standards and Technology

A small gap structure* has been used to study surface chemistry aspects of fluorocarbon (FC) film deposition for FC plasmas produced in a mechanically confined dual-frequency capacitively coupled plasma (CCP) reactor. The small gap structure provides a completely shadowed region without direct ion bombardment, similar to surfaces of sidewalls of trench patterns. On both trench sidewalls and the shadowed surface portions of the small gap structure, very thin fluorocarbon layers are formed by neutral diffusion. The lack of ion bombardment also increases the retention of the chemical structure of the FC film precursors in the deposited films. For C@sub 4@F@sub 8@/Ar, C@sub 4@F@sub 8@/Ar/O@sub 2@ and C@sub 4@F@sub 8@/Ar/N@sub 2@ discharges the deposition rate, composition, and bonding of deposited FC films are determined as a function of processing conditions using ellipsometry and X-ray photoemission spectroscopy. The deposition rate and surface chemistry of FC film deposited in this region depend strongly on discharge chemistry, and atomic force microscopy shows significant nanoscale topography that differs markedly from films produced with simultaneous ion bombardment. The inclinations of feature sidewalls formed for different conditions qualitatively correlate with the deposition rates measured for shadowed surfaces of the gap structure. Results of mass spectrometric investigations are also reported in an attempt to relate the observed compositional differences to radicals produced in the gas phase. @FootnoteText@ * L. Zheng, L. Ling, X. Hua, G. S. Oehrlein, and E. A. Hudson, J. Vac. Sci. Technol. A 23, xxx (2005).

9:40am **PS-TuM5 The Spontaneous Etching of Silicon by F Atoms, Cl Atoms and XeF@sub 2@ : A Unified Model Supported by Experiment and Simulation*, H. Winters,*** University of California at Berkeley*; D. Humbird, D.B. Graves,* University of California, Berkeley **INVITED**

Insights gained from a recent molecular dynamics simulation (denoted HG) are used to refine a model that quantitatively predicts spontaneous etch rates of silicon and explains various experimental observations@footnote 1@ This model is based on the electronic structure of Si and the electron affinity of the incident gas, and assumes that the rate-limiting reaction step is associated with negatively-charged particles in the halogenated Si surface layer. The density of such charge centers in the layer is a function of its thickness and can be calculated using a formalism similar to one previously published.@footnote 2@ HG predicts a ~5 @Ao@-thick SiF@sub x@ layer on undoped silicon exposed to F atoms; XPS data agree with this prediction, and indicate that the layer is about twice as thick for XeF@sub 2 @exposure. Layer thickness is observed via XPS and temperature programmed desorption to be independent of incident halogen flux and temperature over significant ranges of these parameters, also consistent with the HG simulations. Closed-form expressions for the reaction probability of Si (111) as a function of various parameters will be presented. These expressions correlate well with experiments, including reaction probability measurements as a function of temperature (200K--1000 K), dopant concentration (~10@super 15 @ - 10@super 20@ dopants/cm@super 3@), and incident species (F, Cl, and XeF@sub 2@). The model rationalizes the observation that the doping effect in Cl is large relative to F, even though the opposite trend is observed for the spontaneous etch rate. Finally, the HG result that etch products desorb with significant kinetic energy allows modulated beam mass spectrometry data to be quantitatively calibrated, making measured etch reaction probabilities absolute. @FootnoteText@@footnote 1@ D. Humbird and D. Graves, J. Appl. Phys. 96 791 (2004) @footnotes 2@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987) See also erratum @footnote 3@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987)

10:20am **PS-TuM7 Molecular Dynamics Simulations of Ar@super +@ Bombardment of Si: Characterizing Ion-Induced Disorder at Surfaces*, D. Humbird,*** Lam Research Corporation*; D.B. Graves,* University of California at Berkeley*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Previous molecular dynamics (MD) simulations of energetic Ar@super +@ ions bombarding initially crystalline Si surfaces indicated the formation of an amorphous phase of Si on top of crystalline Si. This amorphous phase is established within 1 monolayer of Ar@super +@ fluence, and under continuous bombardment it reaches a steady-state thickness that is a function of the impacting ion energy. We revisit some of these calculations with a different potential energy function that predicts the same general behavior, but also permits accurate simulation of F atoms interacting with a Si surface. We discuss changes to the average Si-Si bond length, bond angle, and other local order parameters as a result of Ar@super +@-induced amorphization. We note sharp transitions of these properties at the interface between amorphous and crystalline Si. Finally, we discuss differences in uptake and etch rate when thermal F atoms adsorb on and spontaneously etch the amorphous and crystalline surfaces. Some parallels are drawn between the simulations and recent real-time ellipsometry and second harmonic generation experiments, which give information on amorphous layer formation, and on bond disorder at the interface and surface of the amorphous layer, respectively.

10:40am **PS-TuM8 Fluorocarbon Polymer Layers and Etching: the Role of Fluctuations, Cluster Ejection, and Redeposition*, J.J. Vegh*[1]*,*** *D. Humbird, D.B. Graves,* University of California, Berkeley

Fluorocarbon (FC) plasma etching is known to result in the formation of a FC-containing 'polymer' film during etch, but the nature of this film remains poorly understood. Understanding and control of this film are essential to meet goals for etch of novel materials (e.g. ultra low-k (ULK) dielectrics) and to minimize photoresist loss and surface roughening during FC plasma etch. Molecular dynamics (MD) simulations of Si etch with FC radicals, F atoms, and argon ions suggest that local film thickness fluctuations are common. These fluctuations result from ejection of clusters of FC (~C@sub 20@F@sub 20@) by Ar@super +@ impacts. Temporary, local thinning of the FC film by cluster removal allows subsequent Ar@super +@ impacts to penetrate into the underlying substrate and facilitate Si etch through the deposition of kinetic energy. Similarly, transport of F atoms to the underlying Si and of etch products to the vacuum are both facilitated by this mechanism. These phenomena have been observed in simulation previously, but the relationships between cluster removal and the formation and persistence at steady state of the fluctuating FC film are not yet clear. This fluctuation effect has not been reported experimentally, to our knowledge. We have collected statistics on the FC clusters formed during etching simulations. We report the relationship between cluster size and composition to various local and instantaneous properties in the near-surface region. These properties include the average FC film thickness and Si etch yield; fluctuations in FC film thickness and surface coverage; incident FC species type and energy; density of the FC film, and incident Ar@super +@ energy. We have simulated cluster re-deposition as well. We conclude that film fluctuation through cluster ejection and perhaps redeposition of clusters play an integral role in the maintenance of the FC overlayer.

11:00am **PS-TuM9 Molecular Dynamics Investigation of the Etching of Passivated SiOCH Low-@kappa@ Dielectric Films*, V. Smirnov*,** *A. Stengatch, K. Gainullin, V. Pavlovsky,* SarovLabs, Russia*; S. Rauf, P. Ventzek,* Freescale Semiconductor, Inc.

Fluorocarbon plasmas are widely used for etching of dielectric thin films (conventional and low-@kappa@) in the microelectronics industry. Fluorocarbon radicals and ions are known to produce a nanometer-scale passivation layer on the dielectric surface, whereupon energetic ion bombardment leads to dielectric material etching. As the passivation films are extremely thin and in-situ monitoring is difficult during etching, very few experimental studies have been able to probe into the fundamental nature of fluorocarbon based etching of low-@kappa@ dielectrics. This paper reports about a computational molecular dynamics (MD) investigation of the etching of SiOCH low-@kappa@ dielectric films by CF@sub x@@super +@ (x=1, 2, 3), SiF@sub x@@super +@ (x=1, 2, 3), CHF@sub x@@super +@ (x=1, 2), and Ar@super +@ ions. The MD model is 3-dimensional and uses the velocity-Verlet method for particle acceleration. Psuodo-potentials for two and three body interactions of Si, O, C, H, F, and Ar have been assembled either using Gaussian based quantum chemistry computations or data available in the literature. The test structures for the MD studies are prepared by starting with crystalline Si and depositing mixtures of SiO@sub x@@super +@, CH@sub x@@super +@ and H@super +@ ions. Film stoichiometry and density can be controlled by means of ion fluxes and energies. A passivation layer is grown on the low-@kappa@ test structures through low energy fluorocarbon ion bombardment. Impact of energetic (100-300 eV) ions on passivated dielectric films is investigated in this paper, and modeling results are used to determine ion etching yields, nature of sputtered clusters, and their energy and angular distributions.

11:20am **PS-TuM10 Scattering Dynamics of Energetic F@super +@ Ions on Si and Al Surfaces*, J. Mace,*** *M.J. Gordon, K.P. Giapis,* California Institute of Technology

Fluorine is a significant component of many processing plasmas. Its reactions with surfaces have been extensively studied in the presence and/or absence of ion bombardment. Yet, little is known about the interaction of energetic F@super +@ ions with fluorinated semiconductor and metal surfaces, perhaps because of the difficulty in conducting well-defined experiments with F@super +@ beams. Using high flux (monolayers/sec) of F@super +@ extracted from an inductively-coupled plasma (ICP) source coupled to a mass-selective beamline accelerator, we have studied the scattering dynamics of 50-1000eV tunable F@super +@ ion beams with Si and Al surfaces. Energy and mass analysis of all scattered products was performed by a triply-differentially pumped electrostatic energy analyzer preceeding a quadrupole mass spectrometer capable of detecting single ions. We observed a transition from elastic to inelastic behavior at 500 and 300eV for Si and Al, respectively, where the directly scattered F@super +@ exits the surface with energy considerably lower than that predicted from binary collision theory due to quantum mechanical effects. At the threshold energy, we observed the onset of F@super ++@ production at considerably lower energy than F@super +@. The inelastic energy losses were attributed to formation of doubly-excited auto-ionizing states of F and F@super +@. In addition, we also saw in much greater yield low-energy (5-20eV) scattered F@super +@, believed to be generated via a stimulated desorption process involving charge transfer to the incident ion from an F atom bound to the surface, leaving the latter in a highly repulsive state. We have also monitored all scattered ionic products as a function of beam energy and identified SiF@super +@ as the dominant fluorinated species emitted from a Si surface, while SiF@sub 2@@super +@ was barely detectable. The implications of these findings for plasma etching and profile evolution will be discussed in the talk.

11:40am **PS-TuM11 IRIS Studies of SiCl@sub x@ Surface Interactions in SiCl@sub 4@ Plasmas*, I.T. Martin,*** *D. Liu, E.R. Fisher,* Colorado State University

Chlorine based plasmas, such as SiCl@sub 4@, are widely used for Si etch processes. Additionally, SiCl@sub 4@/H@sub 2@ plasmas are utilized to deposit a-Si materials. We have characterized SiCl@sub 4@-based plasma systems using LIF, OES, and MS measurements. Density measurements indicate that relative SiCl@sub 2@ densities strongly rely on plasma parameters such as power and pressure. We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of SiCl@sub 2@ radicals with Si substrates in SiCl@sub 4@-based etch and deposition systems. Preliminary data show significant SiCl@sub 2@ surface production (S(SiCl@sub 2@)>2) in all etch systems. These results will be compared to SiF@sub 2@ and CF@sub 2@ IRIS data,

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[1] **PSTD Coburn-Winters Student Award Finalist**

as these molecules are isoelectronic to SiCl@sub 2@. Our results indicate all three molecules behave similarly under etching conditions. Surface interaction data from power, pressure and feed-gas ratio dependence studies will be presented for both etching and deposition plasmas. SiCl@sub 2@ IRIS data will also be compared to previous experimental and theoretical work on SiCl@sub 2@ surface interactions.

Plasma Science and Technology
Room 302 - Session PS-TuA

Dielectric Etch II

Moderator: C. Cui, Applied Materials

2:00pm **PS-TuA1 A New Wafer Level Micro Arcing Mechanism in 90nm CVD Low-K Via Etch on 300mm SOI Substrate***, **H. Cong**, C. Low, R.P. Yelehanka, X. Zhang, C. Perera, W. Liu, J.B. Tan, L.C. Hsia,* Chartered Semiconductor MFG Ltd, Singapore

As semiconductor industry moves to 300mm platform and 90nm technologies and beyond, wafer level micro arcing (WLMA) becomes more frequent in dielectric etch. In this paper, we describe the finding of a new WLMA mechanism and the process regime optimization to prevent it happening. In SICOH via etch, high polymer chemistry is needed for better selectivity to both photo resist and underneath barrier. But on the other hand, a high ion energy plasma is required to achieve a good process widow. The etching tool we used is a 300mm capacitively coupled plasma (CCP) high-gap reactor, which has 60Mhz and 2Mhz RF power source applied on top and bottom electrode individually. During our initial via etch process development, C@sub4@F@sub6@/CH@sub3@F etc.were used as via main etch chemistry for better PR selectivity and striation performance. However, we occasionally encountered WLMA at wafer edge around guard rings. Bare Si wafer was used to check RF parameters during the etch process. Spikes were occasionally observed on lower Vpp and C@sub2@ position traces at the beginning of over etch step. We found that there was a powdery polymer deposited on the upper electrode after main etch step and the plasma instability is irrelevant to incoming material. This WLMA phenomenon is different from the experience on MERIE or CCP low-gap reactor. Therefore, we propose a new WLMA mechanism. In SIOCH via etch, main etch step chemistry generates heavy non-uniform polymer deposition on upper electrode. When the process switches to over etch step (normally high DC bias), the polymer out gassing from upper electrode will introduce non-uniformity e-field in the plasma and it triggers WLMA. New main etch chemistry was developed and proved successful for production. We also compared RF parameters during via etch on both SOI and bulk Si substrate, there is no significant difference with new developed recipe. Wafer full map electrical and KLA defect scanned results show free of WLMA.

2:20pm **PS-TuA2 CD and Etch Front Control with Reduced Plasma Damage in Etch and Ash Processes for Porous low-k Materials***, **R. McGowan**,* SEMATECH*; B. White,* SEMATECH & AMD

We present requirements and methods for improvement of performance in low-k dielectric integrations using various etch and ash processes in back end of line applications. The correct etch and ash chemistry is the key to minimizing surface modifications. The use of porous ultra low-k materials is required to achieve an ultra low keff stack. These materials present new challenges to etch and ash engineers due to their low mechanical strength, porous nature and propensity to plasma damage. Plasma Etch and strip processes cause modifications to the dielectric that reduce the effectiveness of the low-k material. It will be necessary to pick materials with minimal chemical susceptibility to damage, and to develop new etch, ash and cleans processes that cause less damage. We use two layer metal test vehicles. A 90nm CVD (k=2.5) and a 130nm "late poragen burn-out" low-k (k=2.1). This paper presents a discussion on the stack integrations and the etch/ash approaches for each. Both integrations are VFTL (via first, trench last) with no embedded stop layers. Smooth etch fronts through etch and ash steps are key to the integrity of the metal barrier and to reliability performance. We will show the etch and ash chemistries required for each low-k and methods to control plasma damage to the low-k. Polymer deposition and its removal are controlling factors in damage control in the etch/ash processes. An investigation of effects from ash chemistries and reactors for plasma damage and impact on profiles will be presented. Interactions between processes, and their impact on the resulting profiles, will be given. Hardmask chemistries are particularly damaging & methods to damage reduction in these etches will be shown. Data will be presented on the rates and ash rates for ULK materials and the impact of the same process on plasma damage. It is shown that the ash process can be used to smooth the etch front to provide a smoother etch front.

2:40pm **PS-TuA3 Influence of Plasma Modulation on low-k Etching in High Density Fluorocarbon Plasmas***, **V. Raballand**, G. Cartry, C. Cardinaud,* Nantes University, France

Low dielectric constant materials (low-k) are used as interlevel dielectrics in integrated circuits. Materials studied are porous and non porous methylsilsesquioxane polymers (SiOCH), as well as amorphous hydrogenated silicon carbide (SiCH), used as hard mask and/or etch stop layer. We study the influence of bias, and source power modulation on low-k etching in high density CHF@sub 3@ based plasma. In addition, low-k etching mechanisms are investigated by using plasma diagnostics (OES, Langmuir probes) correlated with surface analysis (XPS). We use a 13.56 MHz Inductively Coupled Plasma source mounted above a diffusion chamber where the substrate is biased separately. Etch rates are measured in real time by in-situ multi-wavelength ellipsometry. First, only the bias voltage is pulsed. By decreasing the duty cycle (dc), the threshold between etching and deposition is shifted toward higher bias voltage. Moreover, this threshold common for all materials in continuous mode (around - 40V), is now equal to - 50V for porous SiOCH and - 80V for SiCH when pulsing at 1kHz with dc=0.45. Selectivities exceed 10 on a large bias window (50V), while they only reach 6 in continuous mode. Then, we simultaneously pulse the source power and the bias power. Low-k etch rates and selectivities are measured for various ON-time and OFF-time periods. We observe that when the ON-time period is smaller than the time for the plasma to be in stable regime, selectivities are enhanced. To complete these studies, some pattern transfers are realized and compared in continuous and pulsed modes (pulsed bias, or pulsed bias and plasma). Finally, surface compositions and plasma characteristics are analysed. Etching mechanisms are determined in pulsed and continuous modes.

3:00pm **PS-TuA4 Control of Surface Reactions during Organic Low-k Dry Etching***, **S. Uchida**, M. Hori,* Nagoya University, Japan*; K. Oshima, A. Ando, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan

In the fabrication of Cu/low-k interconnect for 45-nm devices and beyond, precise control of plasma processes becomes indispensable. Hybrid dual damascene structures use organic low-k and SiOCH films for trench and via levels. The N-H-based plasma has been employed to fabricate SiLK@super TM@ trench patterns with high selectivity both to SiO@sub 2@ hard mask and to underlying SiOCH. First, to separate the effects of ion energy and radical compositions, the etching yield of SiLK@super TM@ was investigated by using a beam experiment apparatus with a radical injection system. An Ar@super +@ ion beam (100â?"500eV) was used to irradiate sample surfaces (SiLK@super TM@, SiOCH, and SiO@sub 2@) with supplying N and H radical fluxes. We quantitatively varied both the incident ion energy and the composition of the H/N radical fluxes. H and N radical densities were measured by in-situ vacuum ultraviolet absorption spectroscopy. The threshold ion energy for the SiLK@super TM@ etching was about 100 eV under the condition of H / (H + N) = 11%. The etch yield of SiLK@super TM@ strongly depended on the composition of the radical fluxes. We found that H radicals promoted reactions of N atoms with organic polymers. Consequently, the etch yield of SiLK@super TM@ dramatically increased when a small amount of H radicals (< 20%) were added to the N radicals. This result suggests that the stably controlling of the H radical density in N/H plasma and the incident ion energy in real etching systems is important. The high energy peak of the ion energy distribution function was controlled by adjusting the power and frequency in a CCP system. By decreasing the high energy peak (to decrease the etch yield of the hard mask) while keeping the ion current and etch yield high (to keep a high etch rate for SiLK@super TM@ to decrease the total etch time), we have successfully minimized the erosion of the hard mask and the variation of the critical dimension during SiLK@super TM@ trench fabrications.

3:20pm **PS-TuA5 Modeling of Organic Low-k Etching in a Two Frequency Capacitively Coupled Plasma in N@sub 2@/H@sub 2@***, **K. Ishihara**, C. Shon, T. Yagisawa, T. Shimada, T. Makabe,* Keio University, Japan

The dimension of ULSI device elements continues to shrink in size and multi-layer interconnect system with Low-k materials is employed to reduce RC signal delay in interconnect. We have two main groups of Low-k materials, i.e., organic and inorganic. Low-k materials have distinct characteristics, such as poor mechanical strength and low heat transfer. Under these circumstances, low tempareture plasma source with low damage is practically needed for Low-k material etching. Capacitively coupled N@sub 2@/H@sub 2@ plasma in parallel plate geometry is considered to be the source for organic Low-k material etching. N and H radicals produced in the collision dominated plasma will play important roles on the characteristics of the etching. In our previous work, we have investigated plasma characteristics in N@sub 2@(50%)/H@sub 2@ in two frequency capacitively coupled plasma (2f-CCP) reactor by using VicAddress. In the present study, we have developed the radical transport to the wafer in 2f-CCP by considering the production paths in both gas and surface phases, and obtained the velocity distribution of ions, H@super +@, H@sub 2@@super +@, H@sub 3@@super +@, and N@sub 2@@super +@ incident on the wafer surface. The radical density agrees well with the experimental. Feature profile evolution in a patterned organic Low-k material will be demonstrated in the 2f-CCP reactor in N@sub 2@(50%)/H@sub 2@.

3:40pm **PS-TuA6 Vacuum-Ultraviolet Photon Irradiation Effects in Fluorocarbon Plasmas on SiO@sub 2@ Etching Surface Reactions using In vacuo Electron-Spin-Resonance***, K. Ishikawa,* Tohoku University, Japan*; Y. Yamazaki, S. Yamasaki,* AIST, Japan*; S. Noda, Y. Ishikawa, S. Samuakwa,* Tohoku University, Japan

Using in vacuo electron-spin-resonance (ESR) technique, where the real defect state can be detected without oxidation effect in air,@footnote 1@ surface reactions of fluorocarbon plasma etch of SiO@sub 2@ films were studied. To understand the reaction mechanism on the surface, creation of dangling bonds (DBs) on the surface are indeed a key process. In this study, we investigated the irradiation effects of vacuum ultraviolet (VUV) or ultraviolet (UV) photons on the surface reactions in the plasma etching processes through observation of the DBs creation. Soon after the plasma process, ESR spectra were measured following transferring to the ESR cavity under vacuum ambient. Experimental results showed that DBs are efficiently created by irradiation of plasma emissions such as VUV and UV photons. In fluorocarbon polymer, C-DBs with surrounding F atoms (Hyperfine interaction of 9.1 and 3.4mT.) are created by emissions of CF@sub 4@ plasmas (Intensive radiation in UV range at about 250nm by CF@sub x@). In amorphous fluorocarbon (a-C:F) films, the C-DBs may play roles of enhancement both of adsorption of gaseous CF@sub x@ radicals and of removal itself by bond-breaking in the polymer. On the other hand, Si-DBs (E' center) in the SiO@sub 2@ film are created by irradiation of emissions in VUV range below 140nm (Most of radiation in atomic emissions such as C, F, and Ar). We speculate tentatively that not only reactive species but also plasma characteristics as emissions affect to creation of the DBs, and the created DBs contributes on the surface reactions of the fluorocarbon plasma etching processes, especially employing high density plasmas. @FootnoteText@ @footnote 1@ K. Ishikawa, et al. Appl. Phys. Lett. 81, 1773 (2002).

Plasma Science and Technology
Room Exhibit Hall C&D - Session PS-TuP
Plasma Science and Technology Poster Session

PS-TuP1 Aluminum Nitride formed by Expanding Thermal Arc Plasma Chemical Vapor Depositon*, **G.T. Dalakos**, H. Marek,* GE Global Research Center

This work involves very-high deposition rates of aluminum nitride thin films using a novel, high-density expanding plasma source to dissociate suitable gas-phase precursors. The plasma source is produced from a DC thermal arc discharge that expands into the vacuum deposition chamber, breaking up gas feedstock and forming film precursors. Due to the large, charged species concentration present in the arc source, use of this plasma source allows us to achieve unusually large deposition rates of a few microns/min. In this regard, we discuss the differences between our approach and conventional deposition approaches. We additionally discuss how experimental processing parameters of the expanding thermal arc source affects measured film properties such as composition, morphology and crystalline nature of our deposited films.

PS-TuP2 Study of Deposition Precursors in Amorphous Silicon Nitride Film Deposited by Plasma CVD*, **Y. Ichikawa**, M. Narita,* Fuji Electric Device Technology, Japan*; S. Fujikake,* Fuji Electric Advanced Technology, Japan

To understand the deposition mechanism of hydrogenated amorphous silicon nitride film (a-SiN:H) deposited by plasma CVD, we have studied the deposition precursors and their effective sticking coefficient both in SiH@sub 4@-NH@sub 3@ and SiH@sub 4@-N@sub 2@ gas mixture systems. The a-SiN:H films were deposited on a silicon wafer where a number of trenches with a width of 1μm were formed by etching, and then their film thickness profiles and composition on the trench wall were measured. These experimental results were compared with Monte-Carlo simulation to estimate the species of precursors and their vanishing probability on the deposition surface. The results showed that in SiH@sub 4@-NH@sub 3@ system the dominant precursor is one species (with a vanishing probability of 0.08) and the composition of the film does not vary along the trench wall. On the other hand, in SiH@sub 4@-N@sub 2@ system two species have to be taken into account to fit the simulation with experimental results; one species has a vanishing probability of 0.8 and the other has that of 0.05. Moreover, the composition of the film varies along the trench wall; the ratio of nitrogen to silicon increases with increasing distance from the surface in a trench.

PS-TuP3 Deposition of SiOxNy Films by PE-CVD for OLED Passivation*, **J.H. Lee**, C.H. Jeong, J.T. Lim, J.H. Lim, S.-J. Kyung, G.Y. Yeom,* Sungkyunkwan University, Korea

To prevent the permeation of H@sub 2@O and O@sub 2@ to the devices, the encapsulation of the devices such as metal encapsulation and glass encapsulation are currently used for OLED devices, however, thin film passivation instead of the encapsulation on these devices are preferred for the lighter weight, wider viewing angle, flexibility, etc. Therefore, various permeation barrier materials and various deposition methods for these materials are intensively investigated for the passivation of the next generation flexible flat panel display (FPD) devices such as OTFTs and OLEDs. In this study, bis(tertiary-butylamino)silane (BTBAS) was used as the precursor of Si, SiO@sub x@N@sub y@ thin films were deposited on plastic substrates at a low temperature using a PECVD method and its properties were investigated. BTBAS was used as the precursor of Si because it shows a low impurity content after the deposition and it is safe, easy to handle as a liquid form, and chemically stable compared to other silicon precursors such as SiH@sub 4@, SiH@sub x@Cl@sub y@, etc. Also, by forming multiple layers of SiO@sub x@N@sub y@/parylene, the water permeation properties of the deposited SiO@sub x@N@sub y@ films were also investigated. In this presentation, we will report the deposited film characteristics for an OLED passivation layer such as deposition rate, film crystallization, chemical composition, H@sub 2@O permeation, and optical transmittance measured using an alpha-step, XPS, FT-IR, ellipsometer, and UV spectrometer, respectively.

PS-TuP4 Linearized Process Model Analysis As a Means of Understanding the Behavior of the Reactive Sputtering Process*, **D.J. Christie**,* Advanced Energy Industries, Inc.

Reactive sputtering processes exhibit unique control space behavior which has been effectively explained by mathematical models. The reactive gas partial pressure can have multiple possible values for a range of reactive gas flows which leads to hysteresis in the process control space. A model which effectively explains the process dynamics consists of three coupled non-linear differential equations. Jacobian linearization of the model equations can be used to create a linearized model whose eigenvalues can be determined explicitly.@footnote 1@ Evaluation of the linearized model eigenvalues as a function of reactive gas partial pressure shows the specific partial pressures where hysteresis is likely to occur. In this work, a representative reactive sputtering process is modeled. The small (control) signal analysis and stability are correlated to the reactive gas partial pressure and flow characteristics. In particular, the real and imaginary components of the eigenvalues and the reactive gas flow are evaluated for a realistic range of reactive gas partial pressures. The points where hysteresis is expected to occur based on the two approaches (flow versus pressure, eigenvalues versus pressure) are compared. Insights on process dynamics and potential closed-loop control issues are also extracted from the linear analysis. @FootnoteText@ @footnote 1@ C. Li, J-H Hsieh, Surface and Coatings Technology 177-178, 824 (2004).

PS-TuP6 Stabilization of the Atmospheric Glow Plasma*, **E. Aldea**, P. Peeters,* Eindhoven University of Technology, The Netherlands*; H. de Vries,* Fuji Photofilm B.V*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE.*****Due their huge potential for cost efficient industrial applications uniform atmospheric plasmas (atmospheric glow) attracted a lot of interest in the recent years. Commonly atmospheric glow plasma can be straightforwardly generated only in He or very pure nitrogen and at relatively low power density. It is widely believed that atmospheric glow generation is related to a large pre-breakdown pre-ionization but the link between pre-ionization and atmospheric glow remains debatable. In this paper it is argued that not the pre-ionization but thermal/ionization instability is the key factor, which is preventing the atmospheric glow generation. Excepting He atmospheric plasma generation requires the suppression of the unstable plasma modes. In this way we succeeded to generate the atmospheric glow at high power density and for a large variety of gases. Several dedicated electronic circuits were developed for the suppression of the unstable plasma varieties. The plasma stabilization electronics is exploiting the peculiar low ratio of the dynamic to static resistance of the unstable plasma varieties.

PS-TuP8 Frequency and Dimensional Scaling of Microplasmas Generated by Microstrip Transmission Lines*, **I. Rodriguez**, J. Hopwood,* Northeastern University

A microplasma is generated in a gap formed between the ends of a microstrip transmission line. The microstrip is fabricated in the shape of a circular ring, and the discharge gap is micromachined through the microstrip such that the device resembles a nearly closed C. This geometry resonates if microwave power is coupled to the split-ring at a frequency for which the circumference is one-half of the wavelength. At resonance, a strong electric field is generated in the discharge gap region and a microplasma may be ignited. Split-ring resonator microplasmas operating at 900 MHz have been reported in the literature@footnote 1@ and operate from 0.1 Torr to 760 Torr in air as well as inert gases. The primary advantage of this device in comparison to low frequency and DC microplasmas is the elimination of ion-induced erosion of the micro-electrodes. The ions are not accelerated toward the electrodes because the split-ring is at a constant DC potential. In addition, the ions cannot respond to the microwave field. In this presentation, we report scaling the split-ring resonator. Using an aluminum oxide substrate (@epsilon@@sub r@ = 10.2), the 900 MHz device must be 20 mm in diameter. By increasing the operating frequency to 1.8 GHz, the split-ring resonator is scaled down to approximately 10 mm. Higher frequency operation also improves the confinement of the electrons within the discharge gap by decreasing the amplitude of electron oscillation. The scaled split-ring resonator operates in argon at 1 atm using 0.3 watts supplied by a power amplifier chip from a cell phone. Electromagnetic simulations and measurements of the physical device compare favorably@footnote 2@. @FootnoteText@ @footnote 1@F. Iza and J. Hopwood, IEEE Transactions on Plasma Science, Vol. 31(4), pp. 782-787 (2003).@footnote 2@This work is supported by NSF Grant No. CCF-0403460.

PS-TuP9 Effect of Gas Flow on the Gas Temperature in a High Pressure DC Micro-discharge*, **F. Doll**, Q. Wang, V.M. Donnelly, D.J. Economou,* University of Houston*; G.F. Franz,* University of Applied Sciences, Germany

The gas temperature of a high pressure DC micro-discharge in mostly Ar or He was deduced by spectroscopic measurements of the rovibrational bands of the second positive system of N2, added as a trace species. The micro-discharge was sustained in a slot between two molybdenum electrodes separated by a distance of 200 microns. The gas temperature in He was significantly lower (350-550 K) than that in Ar (over 1000 K), a reflection of the much higher thermal conductivity of He. Increasing the gas flow rate had little effect on the gas temperature in He, but significantly reduced the gas temperature in Ar. This is consistent with the fact that conductive heat losses dominate in the helium micro-discharge, while heat losses by convection play a role in the Ar micro-discharge. The experimental findings were verified with a two-dimensional flow and heat transfer calculation in the micro-plasma reactor. Finally, the cathode temperature was measured with a thermocouple located 1 mm from the face of the electrode exposed to the plasma. The cathode temperature in the Ar micro-discharge was generally less that 400 K. Work supported by DoE/NSF.

PS-TuP10 Plasma-Deposited Silver Containing Nanocomposite Coatings with Bactericidal Properties*, **P. Favia**,* University of Bari, IMIP-CNR, Plasma Solution Srl, Italy*; E. Sardella, M. Nardulli,* University of Bari, Italy*; R. Gristina,* Institute of Inorganic Methodologies and Plasmas (CNR-IMIP) Bari*; R. d'Agostino,* University of Bari, IMIP-CNR, Plasma Solution Srl, Italy

Silver has been considered for centuries for its antibacterial properties,@footnote 1@ that are explained with different mechanisms, including strong interactions with thiol groups of the respiratory enzymes of bacteria. Silver has a broad spectrum of action, from anaerobic bacteria to viruses, yeasts, and fungi. The overuse of silver compounds causes argyria, a discoloration of the skin, often due to the uptake of improperly prepared and unstable colloidal silver. For this reason the interest is often focused on products for topical therapies@footnote 2,3@ instead of systemic, able to release in a controlled way the minimum quantity of silver effective. Nanocomposite coatings (i.e. dispersions of Ag clusters embedded into an organic/inorganic matrix) are under investigation in our lab as silver delivery systems, as alternative to available medical products, since they allow to control the release rate of silver as a function of their chemical composition.@footnote 4,5@ In this work the attention is focused on the ability of such coatings to release a minimum quantity of silver in cell-culture medium without losing bactericidal effect. Coatings have been deposited in RF (13.56 MHz) Glow Discharges fed with a mixture of Diethyleneglycole di-methyl ether (DEGDME) and Ar. Sputtering from the Ag-coated cathode of the reactor occured simultaneously in certain conditions, to give Ag clusters dispersed in the Polyethyleneoxide (PEO)-like coating. Different PEO-like and Ag/PEO-like coatings have been deposited, that have been characterized with different surface analysis techniques. The role of silver and its cytotoxycity in cell culture media has been evaluated with 3T3 Murine Fibroblasts at different time of incubation. The bactericidal effect of Ag+ ions was evaluated with different bacteria. Biological results have been correlated with the quantity of silver released in water at 37°C, as measured with ICP Emission spectroscopy. Acknowledgements: The project MIUR-FIRB RBNE01458S_006, is gratefully acknowledged for funding this research @FootnoteText@ @footnote 1@ Russell et al, Hugo. Antimicrobial Activity and Action of Silver. Prog Med Chem. 1994, 31:351;@footnote 2@ Thomas et al, J Wound Care 2004; 13(9):392;@footnote 3@ Dowling et al, Thin Solid Films 2001; 398-399: 602;@footnote 4@ Favia et al, Plasmas and Polymers 2000, 5(1):1;@footnote 5@ Sardella et al, Plasma Proc. and Polym., 2004, 1:63.

PS-TuP13 Functionalization of Rough Polymer Surfaces and Porous Micron-Sized Beads Using Atmospheric Pressure Plasmas@footnote 1@*, **A.N. Bhoj**,* University of Illinois at Urbana-Champaign*; M.J. Kushner,* Iowa State University

Pulsed atmospheric pressure plasma discharges, such as corona and dielectric barrier discharge devices, are commonly used to functionalize surfaces (e.g., polymer sheets) with the advantages of high throughput and in-line continuous processing. These materials have surface roughness of 100s nm to 10s µm often resulting from the manufacturing process. Porous materials also have highly non-planar surfaces that can be functionalized for novel applications such as drug delivery. In this paper, results from a computational multiscale investigation of atmospheric pressure plasma treatment of rough polymer surfaces and porous polymeric beads are discussed. The investigation was conducted with a 2-dimensional plasma hydrodynamics model using an unstructured mesh capable of resolving a dynamic range of 1000 in spatial scale.@footnote 2@ This capability enables a multi-scale approach in which the reactor scale plasma hydrodynamics and penetration of plasma produced species into surface structures can be simultaneously addressed. A surface kinetics model is integrated with the plasma hydrodynamics model to assess the uniformity of treatment of the surface structures. The model geometry is a dielectric barrier-corona configuration at atmospheric pressure with a gap of a few mm to the surface. Nitrogen-containing gas mixtures produce amine functionalities on rough polymer surfaces and porous polymer beads of 10s µm sizes with pore diameters less than 2 µm. Radicals and ions generated in the plasma diffuse through the pores and access the internal surfaces, a process that depends on polarity of the corona. The uniformity of treatment of the nooks-and-crannies of the rough surfaces and on the internal surfaces of the polymer beads depends on the relative rates of transport and reaction limited processes, and evolves over successive pulses as the surface functionalization is saturated. @FootnoteText@ @footnote 1@ Work supported by NSF (CTS03-15353). @footnote 2@ A. N. Bhoj and M. J. Kushner, J. Phys. D. 37, 2910 (2004).

PS-TuP14 Plasma Simulation for Plasma-based Ion Implantation Sterilization Technique*, **T. Tanaka**,* Hiroshima Institute of Technology, Japan*; M. Tanaka,* PEGASUS Software Inc., Japan*; D. Nakamura,* TWO CELL CO. Ltd., Japan*; H. Fukuyama,* Kobe Steel Ltd., Japan*; T. Takagi,* Hiroshima Institute of Technology, Japan

Plasma-based ion implantation (PBII) sterilization technique is one of the promising sterilization process for three-dimensional work pieces with low temperature, short process time, and no toxic gas. The energy of nitrogen ion used PBII sterilization process with a pulsed negative high voltage (5 usec pulse width, 300 pulses/s, -800 V to -13kV) was estimated using a simple method based on secondary-ion mass spectroscopy analysis of the vertical distribution of nitrogen in PBII-treated Si. The ion energy was calculated based on the depth profile of nitrogen in ion implanted and was low compared to the nitrogen energy calculated based on the voltage applied during processing. It was shown that the experimentally estimated ion energy was at the same level of the value estimated using the plasma simulation. It was shown that the possibility of the design sterilization process and apparatus by using the plasma simulation.

PS-TuP15 Extraction and Collimation of Laser Photoionized Neodymium Ion Beam*, **K.T. Tamura**,* Japan Atomic Energy Research Institute, Japan

Based on the laser isotope separation, ions are produced by the selective photoionization of evaporated atoms. By the effective extraction and collection of these ions, they are considered to be a useful ion source for the applications such as ion implantation. To increase the beam intensity for these applications, a pair of semispherical electrodes was set outside the parallel plate electrodes, and the obtained intensity distributions were measured by scanning a multichannel Faraday cup. Atomic beam of neodymium were generated by electron beam evaporation, and was introduced between electrodes for ion extraction. The atomic beam was photoionized by the irradiation of the third harmonics of YAG laser operated at 10 Hz, and the produced ions were extracted from the electrode. The intensity distributions of the ion beam were detected with a multichannel Faraday cup which has five detection holes arranged horizontally. The distributions were mapped by vertically scanning the detector manually. The vertical and horizontal widths of the ion beam at the detector were reduced by the electric field formed with these electrodes. The central ion beam intensity increased about 36 times compared with that in the case without the additional electric field. The energy spread of the neodymium ion beam corresponded to the potential of the laser photoionized region between ion extraction electrodes. Ions with the central energies of 300~1400 eV were then produced, and it was shown from ion distribution measurements that collimated ion beam was produced for these ion energies. These results show that the application of these electrodes is useful for the extraction and collimation of the laser photoionized ions.

PS-TuP16 Time-Dependent Recombination Reactions of Oxygen Atoms on an Anodized Aluminum Plasma Reactor Wall, Studied by a Spinning Wall Method*, P.F. Kurunczi, **J. Guha**, V.M. Donnelly,* University of Houston

We have studied the pressure, power, and time dependence of recombination of O atoms on an anodized Al surface, using a new "spinning wall" technique. With this method, a cylindrical section of the wall of the plasma reactor is rotated, and the surface is periodically exposed to the plasma and then to a differentially pumped mass spectrometer (MS). By varying the substrate rotation frequency (f), we vary the reaction time, t@sub r@ i.e. the time between exposure of the surface to O-atoms in the plasma and MS detection of desorbing O@sub 2@ (t@sub r@=1/2f). At 600 W and 5 mTorr, the O@sub 2@ desorption signal decreases by a factor of 6 as t@sub r@ is increased from 0.7ms to 40ms. (The signal is zero at f=0.) The O@sub 2@ signal decay rate is highly non-exponential, slowing at longer times. As power is lowered, the signal decreases more strongly at short t@sub r@ than at long t@sub r@. For constant power, signals also decrease at pressures above or below 5 mTorr. The shape of the decay curve is determined solely by the O@sub 2@ desorption signal extrapolated to t@sub r@=0, which is determined by the absolute O flux in the plasma. We have also studied the time dependence of recombination by spinning the substrate at a rapid rate and then turning the plasma on and off. The rate of rise and decay in signal is again highly non-exponential; O@sub 2@ desorption decays by 1/e in ~30ms and is still detectable ~200ms after the discharge extinguishes. When the plasma is turned on, the rise time in O@sub 2@ signal mirrors the decay (~30ms and ~200ms components) if the plasma was recently operated (within the last minute) and is much longer (~2s) if the plasma was off for more than 1 hr, indicating some initial conditioning of the surface. Mechanisms and modeling of O-atom recombination will be compared with these time-dependent results. Supported by ACS-PRF. @FootnoteText@ P.F. Kurunczi - Present affiliation: Varian Semiconductor Equipment, Gloucester, MA 01930.

PS-TuP17 Effect of Coulomb Collision on Oxygen Plasma

K. Nanbu, ***T. Furubayashi,*** Tohoku University, Japan

Plasma processing has been used for fabricating semiconductors. The requirement of high aspect ratio etching is satisfied by using low pressure and high density plasmas. When simulating high density plasmas (n@sub e@ = 10@super 17@-10@super 18@m@super -3@), collision between charged particles should also be taken into consideration. Generally, in simulating plasma using the particle model, we consider only electron-molecule collisions and ion-molecule collisions. In this study, we consider not only such collisions but also electron-electron collisions using Bobylev and Nanbu method,@footnote 1@ because it is most probable that Coulomb collision have effect on the electron energy distribution. We examined the effects of Coulomb collision on plasma parameters. Especially, the effect on electron energy distribution function (EEDF) is important because it influences reaction rate of radicals production and hence, affects the etch rate. The effect of electron-electron collisions on argon plasma was examined previously,@footnote 2@ and we found that there is an effect on electron temperature but little effect on the EEDF. In this study, we simulated oxygen plasma using PIC/MC method considering four species, e@super -@, O@super +@, O@sub 2@@super +@, and O@super -@. The threshold energy of ionization in the collisional events of electron-oxygen collision is much lower than that of argon. So it is expected the electron-electron collisions have large effects on plasma parameters. @FootnoteText@ @footnote 1@ A. V. Bobylev and K. Nanbu, Phys. Rev, E, Vol.61(2000), pp. 4576-4586@footnote 2@ K. Nanbu, T. Furubayashi and H. Takekida, Thin Solid Film(to be published).

PS-TuP18 The Role of Ar Metastables in Distorting Gas Temperature Measurements Derived from Trace N@sub 2@ Optical Emission Rotational Spectroscopy in Ar-Containing Discharges

S.J. Kang, *V.M. Donnelly,* University of Houston

Gas temperature (T@sub g@) is an important parameter in plasma prosessing. One method for obtaining T@sub g@ is to add small quantities of N@sub 2@ to the discharge and determine the rotational temperature (T@sub rot@) of N@sub 2@ from electron-impact induced emission. The assumption is that collisions with electrons transfer the rotational distribution of the ground state intact to the emitting state. Usually the 0->0 and 1->0 vibronic bands of the C@super 3@@PI@@sub u@ -> B@super 3@@PI@@sub g@ transition are observed. We have found that when the plasma contains large amounts of Ar these emissions do not yield reliable values for T@sub g@. For example, in a 98% Ar/ 2% N@sub 2@ inductively-coupled plasma (ICP), these bands yield an apparent T@sub g@ that decreases with increasing power. This erroneous result is due to a second mechanism of N@sub 2@ C@super 3@@PI@@sub u@ excitation by collisions with Ar metastables (Ar*). Kinetic modeling shows that at low powers, this Penning excitation mechanism dominates over electron-impact excitation, while at high power, the converse is true. Penning excitation releases a large amount of energy into N@sub 2@ (C@super 3@@PI@@sub u@) rotations. When this process dominates, the observed T@sub rot@ is very high and greatly exceeds T@sub g@. Consequently, T@sub rot@ decreases with increasing power. When N@sub 2@ emission is observed from vibrational levels above that of Ar (@super 3@P@sub 0@) (11.72 eV), i.e., for v' > 4, Ar* energy transfer is no longer possible. So T@sub g@ derived from the 3->3 vibronic band is lower and increases slightly with power. This trend is more reasonable than the high values and inverse dependence on power from the 0->0 transition, consistent with emission from the 3->3 vibronic band arising only from collision with electrons. Thus the 3->3 band provides a reliable measure of T@sub g@.

PS-TuP19 PLAD Dopant Depth Profile Based on Ion Mass and Energy Distribution for Ultra Low Energy Implantation

L. Godet, *S. Walther, S. Radovanov, Z. Fang, J. Scheuer,* VSEA*; G. Cartry, C. Cardinaud,* Nantes University, France

With standard ion implantation technology, the energy and the mass of the ions striking the wafer are well known and simulations such as Transport of Ions in Matter (TRIM)@footnote 1@ are available to predict dopant depth distribution. During the plasma doping process,@footnote 2@ all the ion species present during the negative voltage pulse applied to the substrate are implanted with an energy spread that is dependent on many plasma parameters. To predict the junction depth and the dopant concentration of a plasma doping implant, the knowledge of the chemical nature of the ion species bombarding the wafer, their energy and their proportion of the total ion flux incident on the wafer are needed. In order to provide this essential information, an ion mass and energy spectrometer is installed below the wafer. The ion mass and energy distributions of the ions striking the wafer with energy range from 250V to 1kV have been measured. Secondary Ion Mass Spectrometry (SIMS) was performed to measure the dopant depth profile under the same conditions. Based on the knowledge of the energy distribution of each species of dopant ion present in the pulsed discharge, a TRIM simulation was performed to model the dopant depth profile in the silicon and compared to SIMS profile. @FootnoteText@ @footnote 1@The Stopping and Range of Ions in Solids, J. F. Ziegler,1985@footnote 2@Plasma Diagnostics in pulsed plasma doping system, B.-W. Koo, IEEE, 2004

PS-TuP21 Characteristics of Inductively Coupled Plasma Source with a Multiple U-Type Internal Antenna for Flat Panel Display Applications

K.N. Kim, *C.K. Oh, G.Y. Yeom,* Sungkyunkwan University, Korea

The development of large-area and/or large-volume plasma source with a high plasma density is desired for various plasma processes from microelectronic fabrication processes to flat panel display device fabrication processes. The plasma sources developed to date for the production of high-density and large-area plasmas are mainly focused on the externally planar ICP. However, scaling up to a conventional spiral-type external plasma sources to a large area sources causes some problems when they are applied to TFT-LCD, and by inserting an antenna into the plasma, more production applicable large area ICP is feasible due to the induction of a strong electric field in the plasma and the efficient power transmission to the plasma. In this study, an internal type large-area plasma source with U-type internal linear- antennas has been proposed as a promising candidate for an efficient high-density plasma source. The characteristics of the plasmas were measured using a Langmuir probe located on the sidewall of the chamber. The results showed a strong dependence of the plasma characteristics such as plasma density and plasma uniformity on the antenna arrangement.

PS-TuP22 Electron Density Measurements with Surface Wave Probes in Magnetized Plasmas

K. Nakamura, Chubu University, Japan*; S. Yajima, H. Sugai,* Nagoya University, Japan

In this paper, the surface wave (SW) probe for measuring electron densities@footnote 1@ was applied to magnetized plasmas, and the characteristics of the SW probe located in parallel to the field were examined experimentally and theoretically under a condition of low plasma density and/or high magnetic field corresponding to magnetron discharges. The experiments were made in inductively-coupled argon magnetized plasmas, and absorption frequencies of the SW probe measured by a network analyzer was examined as a function of the plasma frequency measured by the Langmuir probe. At the low magnetic field, the absorption frequency decreased with a decrease in the plasma, thus proportional to the plasma frequency. However, as the magnetic field increased, a saturation of the decrease in the absorption frequency was observed, especially for the low plasma frequency. The saturated absorption frequency were very close to the electron cyclotron frequency obtained from the applied magnetic field, suggesting that the absorption frequency was seriously affected by the magnetic field under the low density conditions. Actually, plotting absorption frequency @omega@ over cyclotron frequency @omega@@sub c@ as a function of plasma frequency @omega@@sub p@ normalized by @omega@@sub c@, its slope approached to zero with an decrease in @omega@@sub p@/

@omega@@sub c@. This result suggested that the absorption frequency became independent of the plasma frequency as a decrease in @omega@@sub p@/ @omega@@sub c@ and that the density measurements was difficult under the low density and/or high field conditions of @omega@@sub p@/ @omega@@sub c@~0.5. Such a saturation was improved by optimization of dimensions of the probe. Especially, reducing the diameters of the rod antenna and the quartz cover tube of the probe was effective and extended measurable range of @omega@@sub p@/ @omega@@sub c@. @FootnoteText@ @footnote 1@ H. Kokura et al: Jpn. J. Appl. Phys 38 (1999) 5262.

PS-TuP23 Optical Emission Measurements of Dual Frequency Capacitively Coupled Plasmas*, **E.C. Benck**, K.L. Steffens,* National Institute of Standards and Technology

Dual frequency capacitively coupled plasma sources are becoming increasingly important in semiconductor manufacturing processes. By having the two frequencies separated sufficiently far apart, it is possible to essentially independently control the plasma density and ion energies impacting wafers. This significantly increases the operating range and etching control over that of a single frequency CCP. An imaging spectrometer combined with a high speed intensified CCD camera is utilized to obtain spatially and temporally resolved measurements of the optical emissions from dual frequency fluorocarbon plasmas created in a Gaseous Electronics Conference (GEC) reference reactor. Plasma behavior is characterized for a variety of operating conditions. In particular, the influence of a single vs. multiple powered electrodes will be presented.

PS-TuP24 Characterization of an Energetic Neutral Beam Source*, **C. Helmbrecht**, Q. Wang, V.M. Donnelly, D.J. Economou,* University of Houston*; G.F. Franz,* University of Applied Sciences, Germany

The residual ion beam and the energetic neutral beam of a neutral beam source were characterized using an ion energy analyzer in combination with a calorimeter. The beam was extracted through a neutralizer metal grid with high aspect ratio holes separating a 13.56 MHz inductively coupled argon plasma from the differentially-pumped beam characterization chamber. By biasing an acceleration electrode in contact with the plasma, ions in the plasma were expelled through the neutralizer grid, and turned into energetic neutrals by colliding with the internal walls of the holes of the grid. Several Al neutralizer grids were used to study the effect of hole diameter (190-630 microns) and aspect ratio (7:1 and 10:1) on neutralization efficiency and flux. The energy distribution of the residual ions was generally bimodal and the average energy varied in the range of 50-100 eV depending on acceleration voltage and plasma gas pressure. The neutralization efficiency increased with larger holes and higher aspect ratios, approaching complete neutralization of the beam. By assuming that the energy of the energetic neutral beam is approximately the same as that of the residual ion beam, the flux of energetic neutrals was also found. The variation of flux with source operating conditions will be discussed and explained based on plasma molding inside the holes of the grid. Work supported by the Texas Advanced Technology Program.

PS-TuP25 Helicon Discharges with Permanent Magnets*, **H. Torreblanca**, F.F. Chen,* University of California, Los Angeles

Industrial helicon sources have been shown to produce higher plasma densities than unmagnetized ICPs but require the addition of a dc electromagnet and its power supply. This requirement can be obviated by using permanent magnets (PMs). However, injection is a problem, since the field lines of PMs normally do not allow the electrons to leave the source region. Using PMs, we have measured the plasma properties both inside the source and downstream in various helicon discharges, including the Big Blue Mode. To overcome the injection problem, we have tried various types of antennas and various ways to shape the magnetic and electric fields.

PS-TuP26 Discharge Electrode Impedance Effect on Harmonics Generation*, **Y. Yamazawa**, M. Nakaya, M. Iwata, A. Shimizu,* Tokyo Electron AT LTD, Japan

The radio frequency (rf) power is commonly used to excite plasma or biasing the wafer in a plasma reactor for processing of microelectronics materials. Due to the nonlinear behavior of the plasma sheaths, the rf power imposes harmonics of the drive frequency. The generation of the harmonics is of great technological importance, since it contributes significantly to the plasma property and process result. This paper reports the control of the harmonics generation by means of the electrode impedance in a dual-frequency capacitively coupled plasma reactor. The 2nd ,3rd and 4th harmonics of the bias RF frequency were observed to behave with resonant growth by tuning the electrode impedance adequately. A simple nonlinear equivalent circuit model can reproduce the experimental result. A remarkable change in the radial distribution of electron density was observed at the harmonic resonances. This technique can be applied to control the plasma uniformity of the etch chamber. In addition, this technique can be used for reducing chamber-variation by avoiding the unexpected resonance.

PS-TuP27 Electron Beam-Generated Plasmas Produced in Nitrogen and Applications to Materials Processing*, **S.G. Walton**, D. Leonhardt, R.F. Fernsler,* US Naval Research Laboratory*; C. Muratore,* US Air Force Research Laboratory

Electron beam-generated plasmas produced in a nitrogen background have several unique characteristics that make them attractive for materials processing applications that utilize nitrogen species. The US Naval Research Laboratory has developed a plasma processing system that relies on a magnetically collimated, sheet of multi-kilovolt electrons to ionize the background gas and produce a planar plasma. High-energy electron beams are efficient at producing high-density plasmas (n@sub e@ > 10@super 11@ cm@super -3@) with low electron temperatures (T@sub e@ < 0.5 eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 4 eV) at surfaces located adjacent to the electron beam. Of particular interest to nitrogen-based processing applications are the relative concentrations of atomic ions, molecular ions, and radicals, which are significantly different from other plasma sources. Large atomic-to-molecular ion flux ratios (>1) and radical-to-ion fluxes ratios are possible using simple adjustments to system operation, such as substrate position or plasma duty factor. In this work, we discuss in situ plasma diagnostics of pulsed, electron beam-generated plasmas produced in pure nitrogen and nitrogen mixtures. A Langmuir probe and a dual energy/mass analyzer is used to provide a spatio-temporal description of the processing system. The diagnostic results are correlated to the latest results from materials processing applications under study in our laboratory including metal nitriding, reactive sputter deposition, and polymer modification. This work was supported by the Office of Naval Research.

PS-TuP29 A High Density Negative Ion Plasma in a Very High Dielectric-Constant Discharge Tube*, **Y. Ikeda**,* KYOSERA Co. LTD., Japan*; K. Endo, H. Shindo,* Tokai University, Japan

Negative ions in plasmas are much attractive species in material processing, such as ion implantation, CVD and etching in ULSI fabrications. The objective of this work is to study a negative ion plasma source. In particular, an innovative method to produce a negative ion rich plasmas is proposed by employing RF surface-wave plasma with a extremely high dielectric constant discharge tube. As well-known, the surface-wave can only be existed above the resonance density, which depends on the permittivity of the discharge tube. In this work, a negative ion plasma is produced by employing the after-glow appeared in the resonance density of the surface-wave which is enhanced by a extremely high dielectric constant discharge tube. The surface-wave plasmas of O2 and SF6 were produced in a discharge tube by supplying 13.56 and 60 MHz power. The two discharge tubes of a ceramic of TiCa-TiMg, K-140, which is commercially available from KYOCERA Co. and a quartz are employed, and their permittivities are, respectively, 140 and 3.8. The optical emission line measurements were carried out from the lateral view. The axial decay rate of the intensities of the optical emission lines FI in SF6 plasma were 5 times faster in the K-140 discharge tube than in the quartz. In particular, a sudden precipitation of the line intensity could be observed, and this is due to the surface-wave ending at the resonance density, providing a high density after-glow. In O2 plasma, in this after-glow region, the OI emission lines of 777 and 845 nm, which are originated from the mutual neutralization of O- and O+, were observed to be very much enhanced after the sudden precipitation, indicating the rich negative ions populated in this region. While in the quartz discharge tube the line intensity decayed just simply and monotonically. Thus it was concluded that the surface-wave plasma with a extremely high dielectric constant discharge tube was an innovative method of negative ion rich plasma.

Plasma Science and Technology
Room 302 - Session PS+TF-WeM
Plasma Enhanced CVD and ALD

Moderator: M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands

8:20am **PS+TF-WeM1 Developments of Plasma Copolymerization Technique for Deposition of low-k Films***, **K. Kinoshita**, A. Nakano, N. Kunimi, M. Shimoyama, J. Kawahara,* Mirai-Aset, Japan*; O. Kiso, Y. Seino, Y. Takasu,* Mirai-Asrc, Aist, Japan*; M. Komatsu,* Sumitomo Chem., Japan*; K. Nakamura,* Chubu University, Japan*; T. Kikkawa,* Hiroshima Univ., Japan **INVITED**

We have proposed the strategic concept of scalable low-k materials for ULSIs which can be used over two or three technology nodes.@footnote 1@ The major challenge to realize this concept is controlling the dielectric constant and mechanical strength. A plasma copolymerization technique has been developed for this purpose.@footnote 2@ Basic film properties will be determined by the matrix monomer, and modified by copolymerization with modification monomers. A narrow-gap CCP was employed to generate uniform discharge over the 300 mm wafer. A divinylsiloxane-bis-benzocyclobutene (DVS-BCB) was chosen as a starting matrix monomer. The dielectric constant of the polymerized DVS-BCB film was 2.78. Electron density of this polymerization plasma was about 1.5E10 cm@super -3@ as measured by surface wave probe technique.@footnote 3@ Modification monomers were chosen from the view points of the reactivity, the estimated dielectric constant of the monomers, and the vapor pressure. To increase film modulus, phenyl compounds with unsaturated functional groups were introduced. The copolymerization ratio corresponded to the film modulus.@footnote 4@ To reduce dielectric constant, aliphatic compound was introduced. However, copolymerization with DVS-BCB at 400 °C could not reduce the dielectric constant due to decomposition of aliphatic components. A process of low temperature deposition followed by annealing was examined with 2-dimethylvinylsiloxane-tricyclodecane (2DMVS-TCD). A dielectric constant of 2.48 was obtained by deposition at 300 °C followed by annealing at 400 °C. This work was supported by NEDO. @FootnoteText@ @footnote 1@ T. Kikkawa, Ext. Abst. ADMETA 2003: Assian session, Tokyo, 1-2, (2003) 4,@footnote 2@ J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2, (2003) 143,@footnote 3@ K. Nakamura, et al., Proc. Int. Symp. Dry Process 2004, Tokyo, P-29, (2004) 169,@footnote 4@ N. Kunimi, et al., Proc. IITC2004, San Francisco, 8.5, (2004) 134.

9:00am **PS+TF-WeM3 Amorphous Carbon Thin Films Deposition by Pulsed Substrate Biased PECVD using a CH@sub 4@-CO@sub 2@ Gas Mixture***, **G. Gottardi**, N. Laidani, L. Calliari, M. Filippi,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy*; R.S. Brusa, C. Macchi, S. Mariazzi,* Università di Trento, Italy*; M. Anderle,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy

Various plasma-assisted deposition techniques and carbon bearing source materials have been investigated and can be used for the synthesis of a-C:H films. In particular, radio frequency (RF) plasma-enhanced chemical vapor deposition (PECVD) systems are the most common type employed, over a broad range of process conditions which are generally recognized to strongly influence the material properties. This research work intends to explore new perspectives in the hard carbon films production via PECVD, through the use of non-traditional gas precursors (CH@sub 4@-CO@sub 2@) and a voltage pulsing technology applied externally simultaneously to the film growth. The modulation of the substrate bias, when applied in a pulsed mode, provides in fact with more operative opportunities, broadening the process parameters set with respect to the conventional technology with a continuous bias and turning out to be much more effective in the densification and hardening of the material. A multi-technique approach has been used for a thorough characterization of the deposited films in order to highlight the effects of the gas precursor composition and of the ion bombardment due to the substrate bias on the chemical, structural and mechanical evolution of the material. In particular, the chemical composition and the structure were investigated with X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR) and electron energy loss spectroscopy (EELS). Positron annihilation spectroscopy (PAS) was performed for the detection of nano-scale open volume defects while nano-indentation and stylus profilometry techniques were used to evaluate the film hardness and internal stress.

9:20am **PS+TF-WeM4 Multi-hollow Plasma CVD Method for Depositing Cluster-free a-Si:H Films***, **K. Koga**, K. Bando, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

The three major limitations of a-Si:H solar cells are 1) light-induced degradation of cell efficiency, 2) a low deposition rate, and 3) a low cell efficiency. We have developed a multi-hollow plasma CVD method for depositing cluster-free a-Si:H films, since films incorporating less amount of a-Si:H nano-particles (hereafter refereed to as clusters) show better stability.@footnote 1@ For the method, powered and grounded electrode of 70 mm in diameter, which had 24 holes of 5 mm in diameter, were placed at a distance of 2 mm. Discharges were sustained in the holes using a VHF power source. A short gas residence time of ~ ms in the discharge regions suppressed growth of clusters and gas viscous force drives clusters toward the downstream region. Therefore, cluster-free a-Si:H films can be deposited on substrates set in the upstream region. Stability of the films against light soaking was evaluated with their defect density measured by ESR and a fill factor FF of a Schottky cell having a structure of Ni/a-Si:H/n type Si. The initial defect density of a film deposited at 0.12 nm/s is 3.5x10@super 15@cm@super -3@ and that after light soaking (7.5 hours under 2.4 SUN) is 3.7x10@super 15@cm@super -3@. The cell using a film deposited at 0.2 nm/s has a rather high stabilized FF of 0.50 and a small degradation ratio of 2.0 %. A higher deposition rate up to 0.66 nm/s can be obtained by utilizing a higher discharge power. Thus the multi-hollow plasma CVD method is effective in overcoming the three limitations for a-Si:H solar cells. @FootnoteText@ @footnote 1@K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, (2004) 1536.

9:40am **PS+TF-WeM5 Proton/Deuteron Exchange in Functional Plasma Polymer Films (A Neutron and X-ray Reflectometry Study)***, B.W. Muir, **C. Fong**, J. Oldham, P.G. Hartley, K. Mc Lean,* CSIRO, Australia*; A. Nelson, M. James,* Australian Nuclear Science and Technology Organisation

The plasma polymer (PP) deposition of chemically reactive monomers is frequently used to provide a chemical handle on inert surfaces. The characterization of the surface and internal structure of these thin films is critical in establishing their efficacy in technological applications. X-ray and neutron reflectometry are techniques that have become increasingly important in the characterisation of thin-film surfaces and interfaces; it now being possible to obtain angstrom precision depth profiles of a films composition. In this study, we have investigated the physico-chemical properties of allylamine plasma polymer thin films using X-ray and Neutron reflectometry in air and aqueous environments. Correlation of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) data with X-ray and neutron reflectometry measurements on the PP film versus air, has allowed the stochiometric composition of the film to be obtained. The mass density was found to be 1.305 g/cm@super 3@ and film thickness 27.8 nm which correlated well with AFM measurements. Interestingly, when neutron reflectometry measurements are performed in D@sub 2@O we observe a significant increase in the scattering length density of the film from 2.033 e@super -6@ Å@super -2@ in air to 3.81 e@super -6@ Å@super -2@ in D@sub 2@O. By performing contrast experiments in mixtures of D@sub 2@O/H@sub 2@O we have found that a significant proportion of the protons within the film exchange with deutrons from solution. The films were found to contain approximately 3.3% water and 30% of the protons in the film are capable of exhanging, indicating significant functionality within the plasma polymer film. The study demonstrates that rich physicochemical information can be obtained on nano-scale thin plasma polymer films in different environments by combining a number of surface analytical techniques.

10:00am **PS+TF-WeM6 Anisotropic Deposition of Cu and Ru in Trenches by H-assisted Plasma CVD***, **M. Shiratani**, T. Kaji, K. Koga,* Kyushu University, Japan

Previously we realized anisotropic deposition of Cu, for which Cu is filled preferentially from the bottom of trenches without being deposited on their sidewall, by H-assisted plasma CVD using Cu(HFAC)@sub 2@ as a source material.@footnote 1,2@ In this study, we have demonstrated anisotropic deposition of Cu from Cu(EDMDD)@sub 2@ and that of Ru from Ru(ACAC)@sub 3@. Ion irradiation to surface where deposition takes place, is the key to all of the anisotropic deposition processes, whereas deposition characteristics depend on materials. For Cu(EDMDD)@sub 2@ and Ru(ACAC)@sub 3@, the deposition rates on the bottom of trenches decrease with decreasing the trench width, while that for Cu(HFAC)@sub 2@ increases. These results suggest that anisotropic deposition by H-assisted plasma CVD using metal-complex has a potential to be applied to deposition processes of many kinds of metals, metal-oxide, and metal-carbide. We will compare deposition characteristics for Cu and Ru and discuss the deposition mechanisms. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Pure. Appl. Chem. 77(2005)391.@footnote 2@ K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) 1903.

10:20am **PS+TF-WeM7 Metal ALD Challenges in Microelectronics Fabrication*, K. Leeser,*** Novellus Systems Inc. **INVITED**

As device geometries continue to shrink, limitations are encountered with conventional thin film processing techniques. Some of these applications have begun the migration towards atomic layer deposition (ALD) as a means of addressing these limitations. Initial applications have focused on dielectric deposition for DRAM and gate stack, but the migration from fab R&D to production has been slow. Current trends indicate that ALD applications of metallic compounds and elemental metals will actually enter mainstream production at a faster rate than their dielectric counterparts with substantial evaluation activity already at the 45nm node, especially for backend metallization. However, metal ALD process technology, applications, integration, and hardware design are more difficult than those required for dielectric ALD. This presentation will highlight and discuss these critical challenges with emphasis on non-tungsten applications.

11:00am **PS+TF-WeM9 Plasma-assisted Atomic Layer Deposition of TiN Films at Low Substrate Temperatures*, W.M.M. Kessels,*** Eindhoven University of Technology, The Netherlands, Netherlands*; S.B.S. Heil, E. Langereis,* Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* Philips Research Laboratories, The Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with precise thickness control. The extension of the technique with plasma processes (i.e., plasma-assisted ALD) opens up new routes in ALD that are difficult to attain by pure thermal ALD, as for example depositing high-quality films at low substrate temperatures. This is an important issue for metallic films such as TiN. High quality films can be deposited by ALD using the halide precursor TiCl@sub 4@ and NH@sub 3@ but this process is only applicable at temperatures of 350-400 °C. Lower deposition temperatures are, however, necessary for compatibility with some high-k oxides, processes involving Cu to avoid CuCl formation, and for improved barrier properties. Therefore we have developed a plasma-assisted ALD process of TiN using TiCl@sub 4@ dosing alternated with H@sub 2@-N@sub 2@ plasma exposure. The plasma is generated with a remote ICP plasma source and has been characterized by electrical probe measurements and optical emission spectroscopy. In situ spectroscopic ellipsometry has been used to monitor the growth rate per cycle (0.6 Å/cycle at 400 °C) and from a parameter study it has been proven that the surface reactions are self-limiting. TiN films have been deposited for substrate temperatures between 100-400 °C and the material properties have been analyzed by several diagnostics. Some key observations are that the deposition rate decreases and the Cl content and electrical resistivity increase with decreasing temperature. Nevertheless, the Cl content and resistivity remain relatively low for an ALD process. Furthermore, some plasma-related aspects for the ALD process will be discussed, such as facilitated initial growth on different substrates, surface modification of the underlying substrate (nitridation by N radicals), and the influence of wall-recombination of radicals in high-aspect ratio structures.

11:20am **PS+TF-WeM10 Characteristics of HfN deposited by using Remote Plasma Enhanced Atomic Layer Deposition Method*, K.W. Lee,*** *S.J. Han, G.J. Kim, W.H. Jeong, H.T. Jeon,* Hanyang University, Korea

Metal oxide films with high dielectric constants (high-k) have been studied recently to overcome the current disadvantages of SiO@sub2@ material. This high-k oxide material also need to apply new gate electrode because of the problems of polysilicon/high-k gate stacks such as poly-Si depletion effect, Fermi level pinning, surface phonon scattering, high threshold voltages and channel mobility degradation in real devices. Current polysilicon as a gate electrode results in poor transistor performance. Due to these problems new metal gate materials are needed to solve these problems because the metal/high-k gate stack is very effective in screening the phonon scattering and improves the channel mobility. And the use of metal gate electrode eliminates poly-Si depletion effect and Fermi level pinning. Among the many candidates the refractory metal nitrides such as titanium nitride (TiN) and tantalum nitride (TaN) are considered as the solutions to replace current poly-Si gate electrode. HfN exhibits various advantages such as thermal stability, midgap work function(4.65eV), and low lattice mismatch(1.13) with HfO@sub2@ gate dielectric and is considered as one of the most suitable candidates as gate electrode. In this work we studied this HfN material with remote plasma enhanced atomic layer deposition(RPEALD) method with tetrakis-ethylmethylamino-hafnium (TEMAH), Hf[N(CH@sub3@)C@sub2@H@sub5@]@sub4@ as a Hf precursor and NH@sub3@ plasma as a reactant gas. This HfN gate electrode was deposited on the HfO@sub2@ gate oxide. After deposition, the physical and chemical characteristics were evaluated, and MOS capacitors were fabricated with the HfN electrode to measure the electrical properties. The interfacial layers of deposited the HfN/HfO@sub2@ and the TiN/HfO@sub2@ stacks were investigated by high resolution transmission electron microscope (HRTEM).

11:40am **PS+TF-WeM11 Plasma-Enhanced Atomic Layer Deposition for Compositionally Controlled Metal Oxide Thin Films**, *R.M. Martin,* ***K.M. Cross****, J.P. Chang,* University of California, Los Angeles

The need to replace SiO@sub 2@ by a higher dielectric constant material in fabricating smaller and faster metal-oxide-semiconductor (MOS) transistors is well recognized by the National Technology Roadmap for Semiconductors. Atomic layer deposition emerges as a viable chemical processing technique to enable the deposition of ultra-thin and highly conformal thin films, and the use of plasma allows greater flexibility in designing doped or alloyed thin films with controlled compostition. In this work, we discuss the atomic layer deposition of HfO@sub 2@ and Hf@sub 1-x@Si@sub x@O@sub y@ using an alternating, cyclical sequence of hafnium terta-tert butoxide and tetra ethyl ortho silicate as the chemical precursors and oxygen radicals generated from an oxygen plasma as the oxidant. Optical emission spectroscopy (OES) was used to identify and quantify the gas phase atomic species. The thicknesses of the films scaled linearly with the number of deposition cycles as determined by both ellipsometry and x-ray photoelectron spectroscopy (XPS) measurements. Thin film composition of Hf@sub 1-x@Si@sub x@O@sub y@ can be varied and controlled by the chemical sequences, as verified by XPS compositional analysis. Atomic force microscopy (AFM) was used to determine surface roughness of the deposited films as a function of the deposition chemistry sequence and film thickness. MOS transistors were fabricated with the PEALD deposited films and capacitance-voltage (C-V) and current voltage (I-V) measurements showed that the PEALD HfO@sub 2@ films had a dielectric constant of 25 and an equivalent oxide thickness of 12.5-15 Å. Device results of Hf@sub 1-x@Si@sub x@O@sub y@ will be discussed as a function of the Si concentration and the resulting interfacial composition.

Plasma Science and Technology
Room 304 - Session PS-WeM

Advanced Gate Stack Fabrication

Moderator: S. Vitale, Texas Instruments

8:40am **PS-WeM2 Ta Based Metal Gate Etch for Dual Metal Gate CMOS Applications*, C.H. Huffman*,** *Z. Zhang,* Texas Instruments Assignee to SEMATECH*; S.C. Song,* SEMATECH

Although the ITRS states that low power applications may require high-k materials first, the high performance devices trend will soon require both high-k dielectrics and metal gate electrodes to remove polysilicon depletion effects. The selection of the metal gate material will be driven by the workfunction of the metal in order to control the threshold voltage of the transistors. Candidate metals should have a workfunction within 0.1v of the conduction band and the valance band edges for NMOS and PMOS respectively. The potential NMOS candidate metals are more reactive while the PMOS candidates are more noble like and this creates an etch challenge for dual metal CMOS integration. This paper will discuss the formation of dual metal gate CMOS structures using Ta based metal electrodes (TaN, TaSiN, TaCN). Affects of plasma parameters on the various metals will be discussed with respect to successful construction of dual metal gate CMOS. Differences in recipes for the various metals will be compared and contrasted with respect to successful construction of advanced metal gate electrodes. Included in the discussion will be potential process solutions for some of the common multiple material gate etch issues that occur. Optical endpoint control will be included for selected materials and process steps.

9:00am **PS-WeM3 Challenges in Plasma Processing for Advanced Gate Stack Fabrication**, ***B.-W. Chan,*** Taiwan Semiconductor Manufacturing Corp., Taiwan*; Y.-H. Chiu,* Taiwan Semiconductor Manufacturing Corp.*; E. Luckowski, B. Goolsby, S. Rauf, P.J. Stout, B. White, P. Tobin,* Freescale Semiconductor*; H.-J. Tao, S.-M. Jang, M.-S. Liang,* Taiwan Semiconductor Manufacturing Corp. **INVITED**

High gate leakage current limits gate oxide thickness shrinkage in traditional SiO2 dielectrics. New gate stacks with novel material combinations are being investigated to reduce gate leakage while enhancing transistor performance. The combination of high K dielectrics and metal gates is a leading candidate for advanced CMOS gate materials but at the cost of increased complexity and greater challenge for the plasma processes that would be used to etch them. In this presentation, we will point out critical issues related to high K and metal gate etch and in particular dual metal gate fabrication. Examples of how simulation is being used to aid advanced gate etch development will also be presented. A specific focus of the talk will be gate trim process and resultant accurate critical dimension (CD) control and meeting CD control metrics required for beyond 65nm transistor fabrication.

9:40am **PS-WeM5 Challenges in Plasma Etching of Metal Gate Stacks**, ***A. Le Gouil,*** STMICROELECTRONICS*; E. Richard, T. Chevolleau, G. Cunge, O. Joubert, L. Vallier,* LTM (CNRS), France

The rapid downscaling of metal-oxide-semiconductor transistors imposes the introduction of metal gates electrodes and high k gate dielectrics. Hence the patterning of a typical gate stack (Si/metal/high-k) requires the development of new etching processes. In this work the metal gate etching process is developed with both poly-Si/TiN and poly-Si/TaN stack for the gate electrode and HfO@sub2@ or HfSiO (3.5 nm thick) as the gate dielectric. First, the silicon part of the gate is etched using a standard HBr/Cl@sub2@ silicon gate etching process, which is followed by the metal etching step. By comparison with classical silicon etch processes two main issues are identified during the etching of the metal gate stack. First, when silicon etching stops on a metal instead of a SiO@sub2@ layer, a slope is observed at the bottom of the silicon etch profile. This difference is attributed to charging effect: charge accumulation on the insulator gate oxide deviate the ions towards the bottom of the gate (thus eliminating the gate foot), while this does not occur on a conductive metallic layer. Second, in the HBr-rich chemistry that is needed to etch the metal layer selectively towards the gate dielectric, a strong slope is systematically observed in the metal etch profile. This slope is attributed to the continuous increase of the mask dimension during the etching process due to the redeposition of precursors on the mask and feature sidewalls. We will show that these precursors originates from the SiOCl coating formed on the reactor walls during the silicon etching process, and which is subsequently sputtered during the metal etching step. This is a serious issue for critical dimension control in metal gate etching processes, and potential strategies to minimize it will be investigated.

10:00am **PS-WeM6 Investigation of Fluorocarbon Polymer Formation in Polysilicon Etching on Metal Gate**, ***E. Luckowski,*** Freescale Semiconductor, Inc.*; B.W. Chan,* TSMC*; S. Rauf, A. Martinez,* Freescale Semiconductor, Inc.

It is well known that control of critical dimension and profile for ULSI devices with conventional polysilicon gates below the 90-nm technology node requires a detailed understanding of chemical etching and by-product deposition mechanisms in a plasma system. Carbon-containing feedstock gases such as CF4 are typically used in mixtures of Cl2, HBr, and/or SF6 to achieve a balance between deposition and etching required for profile control that also meet selectivity requirements for thin dielectric layers in MOSFET devices. Impact of chamber walls and contribution of species from masking materials can play an important role in the overall balance, as well as other additives such as O2 and N2. For advanced gate stacks, as conventional polysilicon gates are being replaced by metal gates to overcome polysilicon depletion effects, the impact of these various mechanisms on metal gate patterning must also be considered. In this work, we investigated the impact of polymer formation in polysilicon etch processes on the profile of polysilicon/transition metal gate stacks on high-K dielectrics. For fluorocarbon etching in particular, the C/F ratio has been found to strongly impact the final profile of polysilicon/metal gate stacks. OES and in-situ reflectometry were used to characterize composition and changes in the plasma conditions, while polymer formation and etch rate were characterized by SEM/TEM. Plasma modeling was also done using a 2D integrated equipment-feature scale model to improve understanding of the interaction between polysilicon and metal gate etch processes.

10:20am **PS-WeM7 Ion-Enhanced Plasma Etching of Metal Oxides in Chlorine Based Plasma**, ***R.M. Martin,*** University of California, Los Angeles*; H.O. Blom,* Uppsala University, Sweden*; M. Sawkar, J.P. Chang,* University of California, Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium based oxides, for sub-65nm complementary metal oxide semiconductor (CMOS) devices. An electron cyclotron resonance high density plasma reactor is used in this work to study the etching of metal oxides and their corresponding metals in chlorine based chemistries. The plasma density, electron temperature, and gas phase species are characterized by a Langmuir probe, an optical emission spectrometer, and a quadrupole mass spectrometer. The etching of Al@sub 2@O@sub 3@, SiO@sub 2@, and HfO@sub 2@ was first studied in Cl@sub 2@ and BCl@sub 3@ plasmas, to allow for studies of the etching of hafnium aluminate, HfAl@sub x@O@sub y@, and hafnium silicate, HfSi@sub x@O@sub y@, with well controlled and varying compositions of Al and Si in HfO@sub 2@. The dominant etch products of Al and Hf metals in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides and metal boron-oxy-chlorides, respectively. These results enabled the assessment of the effect of metal-oxygen bond strength on the surface etching reactions, as well as the oxygen removal mechanism in the etching of metal oxides. The etch rates of hafnium aluminates were found to increase with the square root of ion energy, and the surface chlorination was enhanced with increasing ion energy, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. The etching selectivity of HfAl@sub x@O@sub y@ and HfSi@sub x@O@sub y@ to Si in Cl@sub 2@ and BCl@sub 3@ plasmas will be presented, with a focus on the effect of increasing concentrations of Al and Si, and how the etch rates compare to the etching of Al@sub 2@O@sub 3@, SiO@sub 2@, and HfO@sub 2@ individually. Finally, the application of a generalized model, developed for the etching of ZrO@sub 2@ and HfO@sub 2@, to the etching of Hf aluminates and silicates in chlorine based plasmas will be discussed.

10:40am **PS-WeM8 ICP Etching of p-type Conducting Materials with High Work Function for CMOS Application**, *W.S. Hwang, Y.Q. Wang,* National University of Singapore*;* ***W.J. Yoo,*** National University of Singapore, singapore*; V.N. Bliznetsov,* Institute of Microelectronics, Singapore

As metal electrode / high-k dielectric gate stacks are expected to be integrated for future complementary metal oxide semiconductor (CMOS) device process, extensive research on new conducting electrodes as a replacement for poly-Si is currently underway. Many candidate materials have already been identified as potential n-type conducting materials in the work function range of 4.0-4.5 eV. However, only a few conducting materials have high work functions above 5.0 eV to replace p-type poly-Si, and thus IrO@sub 2@, Ir, Ni, and Pt which meet this requirement are receiving significant attention as candidates of p-type conducting materials. Plasma etching of these materials is one of the most challenging issues in the integration of advanced CMOS gate stacks because of their chemically inert property. In this work, the etching properties of the p-type conductors / high-k gate stacks are investigated in SF@sub 6@ / Cl@sub 2@ / O@sub 2@ using inductively coupled plasma (ICP). Gas composition and plasma parameters of pressure, source power and bias power were changed to understand the etching mechanisms. The linear dependence of etch rates on the square root of bias voltages obtained from most of the above p-type conducting films indicated the dominance of ion induced etch mechanism in both SF@sub 6@ and Cl@sub 2@ etching. The effect of byproducts generated during etching on surface properties showed two different trends, depending on which type of by-product formation is predominant: volatile or nonvolatile. This phenomenon was well explained by evaporation temperature and Gibbs free energy of formation of byproducts in SF@sub 6@ and Cl@sub 2@. X-ray photoelectron spectroscopy (XPS) also revealed that more residues remain after the Cl@sub 2@ etching than the SF@sub 6@ etching. Using the optical emission of fluorines and other halogenated compounds, we were able to control the etch endpoints from the gate stack using p-type conducting materials.

11:00am **PS-WeM9 Damage-free MOS Gate Electrode Patterning on Thin HfSiON Film Using a Neutral Beam Etching**, ***S. Noda,*** *T. Ozaki, S. Samukawa,* Tohoku University, Japan

We have already reported that our newly developed neutral beam could realize highly anisotropic gate electrode patterning on thin SiO@sub 2@ film with reasonable etching rate and etching selectivity.@footnote 1@ In this paper, radiation damages during the gate electrode patterning on thin HfSiON gate dielectric films (2nm) were investigated in our system. By changing the beam acceleration method (DC or RF voltages) in the neutral beam source, the beam flux and its composition (ratio between neutral and charged particles) could be controlled on the surface. Then, the leakage current of gate dielectric film was measured with antenna MOS capacitors. Although the gate leakage currents of the MOS capacitors measured just after the etching of poly-Si electrodes slightly increased in any conditions, its values were sufficiently lower (less than 1/10) than that in a conventional plasma etching. Since the leakage current increased according to over etching time, it was understood that a little degradation was caused by small stress current through the thin gate dielectric films due to the residual charges even during the neutral beam etching process. However, the residual charge current was extremely low and degradation of the gate dielectrics was negligibly small even if annealing was not performed in the neutral beam process. @FootnoteText@ @footnote 1@S. Noda et al., JVST A22,1506 (2004).

11:20am **PS-WeM10 Evaluation of Several Plasma Etching and Boron Cleaning Processes for Hafnium Oxide Thin Films on Silicon***, **C. Wang**, V.M. Donnelly,* University of Houston

At present, BCl@sub 3@-containing plasmas are commonly used to etch high dielectric constant ("high-k") materials such as HfO@sub 2@ and aluminum oxide. However, a boron residue is left on underlying surfaces during the overetch period. Boron is a p-type dopant; its presence is undesirable in subsequent processing. Previously, we reported that pure H@sub 2@ plasmas were effective in removing B from Si surfaces after HfO@sub 2@/Si and Al-oxide/Si samples were overetched in high density BCl@sub 3@ plasmas for 60 s. The underlying Si substrate, however, was etched about 15 nm. Here we report that dilute H@sub 2@/Ar plasmas (1 to 5% of H@sub 2@) are also effective in removal B, but in a more controlled fashion, such that the etching of the Si substrate can be minimized. After 60 s overetch in BCl@sub 3@ plasmas, HfO@sub 2@ samples were transferred under vacuum to an ultrahigh vacuum (UHV) for X-ray photoelectron spectroscopy surface analysis. B deposited during BCl@sub 3@ plasma etching was removed from the reactor walls in a pure H@sub 2@ plasma, and the samples were then returned to the plasma chamber and exposed to a dilute H@sub 2@/Ar cleaning plasma, and then re-examined by XPS. Under the best conditions (1% H@sub 2@/Ar plasma), > 90% of B was removed from Si in 20 s, while etching away

11:40am **PS-WeM11 Damage-free Ultrathin Oxynitride Films Formed Using Pulse-Time-Modulated Nitrogen Plasma***, **S. Fukuda**, C. Taguchi, Y. Kato, Y. Ishikawa, S. Noda, S. Samukawa,* Tohoku University, Japan

Ultra thin Si oxynitride (SiO@sub x@N@sub y@) films have been identified as leading candidates to replace conventional SiO@sub 2@ gate dielectrics for present and future ultra large-scale integrated circuits. Remote plasma processes for top surface nitridation of thermally grown oxides have been developed and applied in complementary MOS device applications. However, it is much difficult to control the concentration and position of nitrogen in ultrathin Si oxynitride film by using plasma processing and there are many serious problems, such as plasma radiation damage and increases in interface state density due to N penetrating the SiO@sub 2@-Si interface. To overcome these problems, we have already proposed pulse-time-modulated (TM) plasma nitridation.@footnote 1@ The pulsed nitrogen plasma makes it possible to restrain injection of higher energy particles from plasma into the silicon dioxide film. Then, the concentration and position of nitrogen in ultrathin Si oxynitride film could be controlled by changing the pulse-on time in the TM N@sub 2@ plasma. Additionally, the TM plasma could drastically reduce the UV and VUV photon radiation damages to Si oxynitride film, because of low electron energy during pulse-off time in the TM plasma. As a result, by using the TM plasma nitridation, NBTI characteristics were about 200 % improved at the maximum. TM plasma is very promising candidate as the damage-free nitridation method for SiO@sub 2@ and high-k films. @FootnoteText@ @footnote 1@ S. Samukawa, Y. Minemura, and S. Fukuda, Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L795-L797.

Plasma Science and Technology
Room 302 - Session PS-WeA

Atmospheric Plasmas and Microdischarges

Moderator: L. Bardos, Uppsala University, Sweden

2:00pm **PS-WeA1 Limitations for Replacement of Low Pressure Plasma by Atmospheric Pressure Plasma**, ***D. Korzec,*** German University in Cairo - GUC, Egypt **INVITED**

A substantial research effort in recent years was focussed on the development of atmospheric pressure plasma (APP) for technological applications. For some applications such as surface treatment or rapid film removal the technological progress is fast and processes are available, being an alternative for the well established low pressure plasma approaches. For other applications, such as high quality film deposition or anisotropic structuring, the application of APP faces serious difficulties. These problems are discussed from the point of view of fundamental physical limitations. The different type of pressure scaling rules are critically reviewed, leading to the conclusion that APP works not because of scaling, but because of specific physical phenomena, which are significant in the pressure range over 100 Torr but can be disregarded for lower pressures. Special focus will be on the dynamics of the APP discharges and effective life times of species used for driving the APP processes. In this context, the frequency ranges for APP generation are investigated. It is shown, that only very narrow parameter windows and only selected gas mixtures allow the successful processing. Different types of APP discharges will be analyzed from the point of view of the basic physical limitations. Conclusion from this analysis will be the estimation of future trends in technological applications of APP and the definition of realistic process challenges.

2:40pm **PS-WeA3 Cold Atmospheric Plasma in Nitrogen and Air Generated by the Hybrid Plasma Source**, ***H. Barankova***, *L. Bardos, D. Söderström,* Uppsala University, Sweden

Generation of long plumes of cold atmospheric plasma in nitrogen and air has been successfully performed by the Hybrid Hollow Electrode Activated Discharge (H-HEAD) source. The source with a simple cylindrical electrode terminated by a gas nozzle combines the microwave antenna plasma with the hollow cathode plasma generated inside the gas nozzle by pulsed DC power. The H-HEAD source is capable to generate up to 10 cm long plumes in air at the microwave power below 500 W and at air flow rate as low as 100 sccm. Corresponding flow rates in nitrogen plasma are even less than 80 sccm. The discharges in air and nitrogen have similar shapes and are comparable with corresponding plasma columns in argon. Comparison of optical emission spectra of the plasma in nitrogen and air are presented. Temperatures generated on steel substrates by interaction with nitrogen and air plasma columns at different microwave and DC powers are compared with corresponding effects in argon plasma.

3:00pm **PS-WeA4 Ultra Fast Surface Modification Processes Employing Compact Non-Equilibrium Atmospheric Pressure Plasmas**, ***N. Yoshida,*** Fuji, Machine Mfg. Co., Ltd., Japan; *H. Kano,* NU-EcoEngineering, Japan; *S. Den,* Katagiri Engineering Co., Ltd, Japan; *M. Hori,* Nagoya Univ., Japan

In the atmospheric pressure plasma processing, the vacuum facilities are basically not needed and the plasma chemistry with considerably large amount of radicals can be utilized. Consequently, the high-speed material processes such as etching, deposition and surface treatment will be potentially realized employing atmospheric pressure plasmas and the equipment cost can be drastically reduced compared with other plasmas. Up to now, many generation technologies of atmospheric pressure plasma have been proposed. We have developed the compact non-equilibrium atmospheric pressure plasma employing new type of micro-hollow cathodes. This device was constituted of the electrode with double micro-hollow structures, which is a very compact size of several ten micrometers and very light weight. Furthermore, it enables to generate the stable plasma in the atmospheric pressure condition. In this study, this plasma was generated with supplying voltage to two special hollow cathode electrodes, and throwing the argon gas of 500ml per minute into the both electrodes. The atmospheric pressure plasma generation can be realized not only in argon but also in air. When this plasma was irradiated on the glass surface for a short time, the considerable change was observed on the surface of the glass. XPS analysis indicated that the C-O bond on the glass surface was drastically decreased while a new peak of O=C-O bond appeared during the plasma irradiation. After only 0.08 seconds irradiation, the contact angle of 20 degree was obtained and after 0.4 seconds, that of 8 degree was easily realized. Therefore, the high hydrophilic processing was successfully achieved in a very short time by using this plasma. From these results, the compact non-equilibrium atmospheric pressure plasma developed in this study will be very promising for a lot of applications to various kinds of surface treatment fields.

3:20pm **PS-WeA5 Design, Diagnostics, and Applications of Microplasmas Operated at around Atmospheric Pressure**, ***K. Tachibana,*** Kyoto University, Japan **INVITED**

Recently, microplasmas of sub-millimeter to micrometer scales are of much interest for various applications such as displays, light sources, micro total analytic systems, micromachining tools, and so on. Microplasmas can be operated not only as a sole device but also in one or two dimensional arrays. In addition, those are operated at a higher pressure range, including atmospheric pressure, according to the shrinkage of the sizes. These features make their potential larger for wider applications. If we use gas discharges for the generation of microplasmas, the electrode configuration is categorized as counter, coplanar, and coaxial electrode types. The dielectric barrier discharge (DBD) scheme is also advantageous in their parallel operation in arrays, where electrodes are covered by dielectric materials for preventing the current concentration automatically thanks to the accumulated surface charge. As the first example, several types of microdischarges are introduced which are used in plasma display panels. Experimental results on spatiotemporal behaviors of microplasmas in unit discharge cell are explained, where the excited species have been diagnosed by using a laser absorption spectroscopy method and the electron density by a mm-wave transmission technique. Those results are discussed for the improvement of luminous efficiency. As the second example, a coaxial mesh-type DBD with a microplasma integrated structure is explained as a large area plasma source for the purpose of various surface treatment technologies. The superior performances are explained in a comparison with those of a conventional parallel plate DBD system for the wider parameter ranges of stable operations. As the third example, our new idea of microplasma devices for the control (switching, filtering, etc.) of microwaves will be explained by using the dielectric properties of plasmas. This idea can be expanded towards microplasma photonic crystals.

4:00pm **PS-WeA7 A Non-Equilibrium Atmospheric Pressure Plasma Operating at High Power Densities**, ***M. Moravej,*** University of California, Los Angeles; *X. Yang,* Researcher; *J. Penelon, S. Babayan,* Surfx Technologies; *R.F. Hicks,* University of California, Los Angeles

A new atmospheric pressure plasma source has been developed that shows exceedingly high processing rates. For example, kapton films have been etched at 5.0 mm/s using an argon and oxygen discharge with 6.0 vol.% O2 and a temperature of 280 Â°C. The plasma source consisted of a small quartz tube that was capacitively coupled to radio frequency power at 13.56 MHz. The input plasma power could be increased up to 150 W/cm3 without arcing, or forming a streamer like discharge. At this power density, the gas temperature was determined by spectroscopic methods to be 300Â±30 Â°C. The O atom concentration was measured in the plasma afterglow by nitric oxide titration, and was found to be 1.2Â±0.6 Â´1017 cm-3 at 150 W/cm3 and 6.0 vol.% O2 in Ar. This corresponds to 15% dissociation of the oxygen molecules fed to the source. The concentration of ozone in the downstream region equaled 4.3Â±0.5 Â´1014 cm-3, as determined by UV absorption spectroscopy. These results were found to be in good agreement with a numerical model of the plasma and afterglow that included the reaction mechanism and the plasma electron density and temperature as calculated from current-voltage measurements. At the meeting, we will discuss the physics and chemistry of this new atmospheric plasma in detail. We will also present results on materials processing with this device, such as silicon dioxide etching and/or thin film deposition.

4:20pm **PS-WeA8 Modeling of Pulsed Microdischarges for use as Thrusters@footnote 1@**, ***R.A. Arakoni,*** University of Illinois at Urbana-Champaign; *J.J. Ewing,* Ewing Technology Associates; *M.J. Kushner,* Iowa State University

Microdischarges having characteristic dimensions of 100s of µm with back pressures of 10s to 100s of Torr are being investigated for use as sources of thrust for small satellites. These devices are capable of generating up to mN of thrust using noncontaminating propellants such as rare gases. The class of device of interest is a cylindrical discharge operated in dc or pulsed modes. The bore of the discharge is fabricated in a heat-resistant ceramic with micro-fabricated ring electrodes. The dominant mode of propulsion is thermal heating of the neutral gas by the discharge, primarily by charge exchange. In this talk, this class of microdischarge will be computationally investigated using a 2-dimensional plasma hydrodynamics model having an unstructured mesh to resolve non-equilibrium electron, ion and neutral transport using fluid equations.@footnote 2@ Sheath accelerated, beam-like electrons are resolved using a Monte Carlo simulation. A compressible Navier-Stokes module provides the bulk fluid velocities and temperatures. Changes in surface properties are addressed with a surface site-balance model. Results from a parametric investigation of back pressure (a few 10s to 100s of Torr), power, and pulse length will be discussed for rare gas mixtures with the goal of maximizing the velocity of the exhaust at the exit plane. Velocities of up to 100s m/s have been predicted in the throats of the devices with plasma densities of 10@super 13@ - 10@super 14@ cm@super -3@ with back pressures of 50 Torr in a cw operation mode. Since the source of propulsion is plasma heated gas, the siting of the plasma within the bore of the microdischarge, and subsequent heat transfer to the walls, is an important design consideration. @FootnoteText@ @footnote 1@ Work supported by Ewing Technology Associates, NSF (CTS03-15353) and AFOSR. @footnote 2@ A. N. Bhoj and M. J. Kushner, J. Phys. D, 37, 2910 (2004).

4:40pm **PS-WeA9 Atmospheric Microplasma-on-a-Chip Operating in Air***, **J. Hopwood**,* Northeastern University*; F. Iza,* Pohang University of Science & Technology, Korea

In this paper, an atmospheric pressure plasma-on-a-chip operating in air is described. The microplasma is ignited and sustained by microwave power (900 MHz, 3 watts) from a common cell phone power amplifier. The discharge is sustained within a 25µm gap formed in a microstripline split-ring resonator. The microstrip transmission lines are surface micromachined on a 22 mm diameter aluminum oxide wafer using electroplated copper and gold. The high quality factor (Q) and narrow discharge gap of the split-ring resonator result in electric field strengths in excess of 10 MV/m prior to plasma ignition. The discharge appears as an intense filament, but is not in thermal equilibrium as the measured rotational temperatures for the second positive system of nitrogen are 500-700 K in atmospheric pressure air. The impedance of the microplasma is found by measuring the microwave reflection coefficient of the resonator as a function of frequency. From the plasma impedance, the electron density is found to be on the order of 10@super 14@ cm@super -3@ in atmospheric pressure argon. Lifetime testing shows that the micro-electrodes are not eroded by ion bombardment after 100 hours operating in air at 3 watts. Applications for this microplasma include portable chemical analysis by optical emission spectrometry and ion mobility spectrometry. This work is supported by the NSF under Grant No. DMI-0078406.

5:00pm **PS-WeA10 Diagnostics and Simulations of a Helium Micro-Discharge at Atmospheric Pressure***, **Q. Wang**, D.J. Economou, V.M. Donnelly,* University of Houston*; I. Koleva,* University of Sofia

Spatially resolved measurements (resolution ~ 6 µm) were taken across an L=200 µm slot-type discharge in an atmospheric pressure direct current helium microplasma. Gas temperature profiles were determined from N@sub 2@ emission rotational spectroscopy. Stark splitting of the hydrogen Balmer-@beta@ line was used to investigate the electric field distribution in the cathode sheath region. Electron densities were evaluated from the analysis of the spectral line broadenings of H-@beta@ emission. The gas temperature was between 350 and 550 K, peaking nearer the cathode and increasing with power. The electron density in the bulk plasma was in the range 4-7 x 10@super 13@ cm@super-3@. The electric field peaked at the cathode (~60 kV cm@super -1@) and decayed to small values over a distance of ~ 50 µm (sheath edge) from the cathode. These experimental data are in generally good agreement with a self-consistent one-dimensional model of the discharge. The influence of gas heating on the discharge properties (such as current-voltage characteristic, cathode and anode sheath profiles), was also investigated. As the discharge current increased, the simulations indicate that the anode sheath turned from a positive ion sheath to an electron sheath, with concomitant changes in the sheath electric field profile and direction. This can be explained, based on the balance of charged particle gain and loss. Gas flow does not have a significant effect on gas temperature because of the high thermal conductivity of helium.

Plasma Science and Technology
Room 302 - Session PS+MS-ThM
Process Equipment Modeling

Moderator: D.J. Economou, University of Houston

8:20am **PS+MS-ThM1 Particle Modeling of Plasmas and Gases in Materials Processing*, K. Nanbu,*** *T. Furubayashi,* Tohoku University, Japan **INVITED**

The use of low gas pressure is a recent trend in plasma-assisted materials processing. The low gas pressure means that the collision frequency between two species are insufficient to recover the equilibrium in the velocity distributions. In such a case the particle modeling of plasmas and gases has more sense. First, it is shown that the particle modeling is a solution method of the Boltzmann equation. This gives the theoretical basis of the DSMC (direct simulation Monte Carlo method) for neutral gases and the PIC/MC (particle-in-cell Monte Carlo method) for plasmas. Second, the state-of-the-art modeling is discussed by introducing the problems thus far solved. Last, the results of two newly solved problems are given to show the feasibility of the particle modeling. One is the complicated gas flows in an etching apparatus, consisting of source gases Ar, C@sub 4@F@sub 6@, and O@sub 2@, radicals CF@sub 2@ and C@sub 3@F@sub 4@, and by-products SiF@sub 4@ and CO. The second is the self-sputtering of copper target. The species in the sputtering apparatus are electrons, ions, and sputtered atoms. Here we propose a method to simulate all these species simultaneously even though the velocity difference among species is disparate. This is the first application of the particle modeling to the problem where the slow neutral species are taken into consideration together with charged particles.@footnote 1@ @FootnoteText@ @footnote 1@ K. Nanbu, IEEE Trans. Plasma Science, Vol. 28 (2000), 971-990.

9:00am **PS+MS-ThM3 Coupled Analysis of Inductively-coupled CF@sub 4@ Plasmas and Radicals Flow*, H. Takekida,*** *K. Nanbu,* Tohoku University, Japan

Inductively-coupled CF@sub 4@ plasmas are widely used for the etching of oxide films. In the present work, plasma and flow in an inductively-coupled CF@sub 4@ plasma reactor are simulated simultaneously. The plasma structure and the production rates of CF radicals are examined using the Particle-in-Cell Monte/Carlo (PIC/MC) method. We included low frequency wafer biasing in the plasma simulation. The radicals flow is examined using the direct simulation Monte/Carlo (DSMC) method for which the production rate of CF@sub x@ radicals is the input data from the plasma simulation. The etching reaction on the oxide wafer and the etch products are taken into consideration in the DSMC. After the flow simulation is finished, plasma simulation is improved using the spatial distribution of background CF@sub 4@ gas which is derived from the flow simulation. We repeated a set of these plasma and flow simulation until we obtain a convergence. We compare the results with the ones where the density of background gas CF@sub 4@ is assumed to be uniform. We clarified the effect of gas flow on the CF@sub 4@ plasma structure by the use of coupled analysis. We have found that the radicals flow has a large effect on the spatial distribution of plasma density.

9:20am **PS+MS-ThM4 Effects of an Insulating Focus Ring on a Uniformity of Radical/Ion Distributions in a Wafer Interface in a 2f-CCP Etcher*, T. Yagisawa,*** *T. Makabe,* Keio University, Japan

Technological improvement in efficiency of reactive ion etching of oxide film is still a main issue in plasma etching under the circumstances that the size of the wafer has been continuously increasing from 100 mm in diameter in 1975 to 300 mm in 2003, as well as the miniaturization of ULSI. The etch rate of SiO@sub 2@ in a fluorocarbon plasma is a function of the mixture between the accumulation of radical species on the surface and the impact energy of ions incident on the wafer. Through a series of numerical studies by using VicAddress in addition to the experimental ones, we have demonstrated that a 2f-CCP (two-frequency Capacitively Coupled Plasma) driven by VHF (100 MHz) and LF (1 MHz) sources at each of electrodes has the plasma structure and characteristics appropriate for dielectric etching. That is, in a well designed 2f-CCP, VHF source is prepared to produce a high density plasma and LF source for a high energy ions incident on the wafer. We have confirmed that the radial variation of etch profile is mainly caused by the strong distortion of the surface potential at the wafer edge. In the present study, the influence of the geometry (width and height) and the dielectric constant of the focus ring in SiO@sub 2@ etching has been investigated in CF@sub 4@(5%)/Ar from the viewpoint of the ion velocity (energy and angle) distribution and the radical flux incident on the wafer as a function of radial position. The effective area of the wafer to be processed will be improved by the design of the interfacial physical structure between the surface and the bulk plasma.

9:40am **PS+MS-ThM5 Simulation in Advanced Dielectric Etch Equipment Design and Process Tuning*, K. Bera,*** *D. Hoffman, G.A. Delgadino, J. Carducci, Y. Ye, S. Ma,* Applied Materials, Inc.

Plasma and flow simulations have played vital roles to guide an advanced dielectric etch equipment design and process tuning to achieve desired process performance. Plasma simulation has been performed to study frequency effect on electron density, power deposition and dissociation fraction for a capacitively coupled discharge. Simulation results demonstrated that plasma generation efficiency enhances with increase in frequency while energy of the bombarding ions diminishes. A very high frequency source has been developed to generate high density plasma while RF bias has been used to control ion energy. Charge Species Tuning Unit (CSTU) tunes plasma density and ion flux distributions, and consequently the etch rate uniformity. Using flow simulation we evaluated species residence time that decides the extent of species dissociation in the process chamber. The gap between the showerhead and the wafer was optimized to achieve sufficient dissociation while minimizing the impact of flow convection on the wafer. Flow simulation also guided equipment design for high conductance over a large process window, and for azimuthal flow uniformity using a side pump. Using flow simulation we guided Neutral Species Tuning Unit (NSTU) design that can tune pressure and neutral flow distributions to the wafer, hence, CD bias and profile uniformities. The independent controls of plasma density and ion energy, and distributions of neutrals and ions played crucial roles in process development and tuning that are important for a production-worthy advanced dielectric etch equipment design and process tuning.

10:00am **PS+MS-ThM6 Effect of Reactor Geometry on Ion Energy Distributions for Pulsed Plasma Doping (P@super 2@LAD)@footnote 1@*, A. Agarwal,*** University of Illinois at Urbana-Champaign*; M.J. Kushner,* Iowa State University

Ultra-shallow junctions (USJ) are required for fabrication of sub-0.1 µm transistors in semiconductor integrated circuits. Plasma implantation methods such as pulsed plasma doping (P@super 2@LAD) present simple, low cost alternatives to beam line technologies. P@super 2@LAD is capable of delivering high dose rates at ultra-low energies (0.02-20 keV) using conventional plasma processing technologies.@footnote 2@ In this talk, results from a computational investigation of P@super 2@LAD using different reactor geometries will be discussed. The investigation was performed using a modified version of the Hybrid Plasma Equipment Model to address quasi-dc pulsed biases.@footnote 3@ An inductively coupled plasma is used to generate ions in pressures of 10s mTorr. A quasi-dc pulsed bias is applied to the substrate to accelerate ions. Typical bias pulse lengths range between 5 and 50 µs and bias voltages are up to 20 kV. Results will be presented for Ar/NF@sub 3@ (a surrogate for Ar/BF@sub 3@) gas mixtures. The large bias voltages and long pulse lengths result in there being considerable thickening of the sheath during the pulse. Sufficient charge is extracted during the pulse that some amount of depletion of ions results. Non-uniformities in plasma density as the sheath extends into the plasma or the ability of the plasma to repopulate depleted charge can have a significant effect on the ion energy distributions (IEDs) to the substrate, which influences the doping profiles. For example, at sufficiently high biases (>2 kV), the IEDs can be skewed in the direction of the source of ion production with the result that the ions approach the substrate preferentially from one direction. As the sheath expands into the center of the reactor where the plasma density is higher, the rate of expansion slows. The result can be a laterally dependent sheath thickness which in turn affects the collisionality of ions crossing the sheath. The consequences of varying reactor aspect ratios and positioning of coils on IEDs will be discussed. @FootnoteText@ @footnote 1@ Work supported by VSEA, Inc. NSF (CTS03-15353) and SRC. @footnote 2@ S. B. Felch, B. -W. Koo, R. B. Liebert, S. R. Walther, and D. Hacker, Surf. Coatings Technol., 156, 229 (2002) @footnote 3@ A. Sankaran and M. J. Kushner, J. Vac. Sci. Technol. A, 22, 1242 (2004)

10:20am **PS+MS-ThM7 Computational Modeling of Process Induced Damage During Back End of Line Wafer Processing*, S. Rauf,*** *M. Rasco, A. Haggag, R. Chatterjee, M. Moosa, K. Junker, P. Ventzek,* Freescale Semiconductor, Inc.

A variety of back end of line (BEOL) processes can subject ultra-thin gate dielectrics in transistors to extremely large electric fields or currents. These processes include plasma etching, plasma enhanced deposition and electron beam treatment of low-@kappa@ dielectrics. A computational modeling infrastructure is described in this presentation that is being used to address process induced damage issues for BEOL microelectronics manufacturing processes. The model couples simulations of plasma etching and electron beam processes to an electrostatic model for charging of gate dielectric. The 2-dimensional models for capacitively and inductively coupled etching plasmas are fluid-based and take account of the detailed plasma chemistry of etching plasmas. The electron beam process is simulated using a 1-dimensional Monte Carlo model. The 2/3 dimensional electrostatic model solves the coupled set of Poisson equation and current continuity equation. Dielectric and semi-conducting properties of materials are taken into account in the electrostatic model using nonlinear electric-field dependant conductivity. Computational results show that, if the gate dielectric is exposed to current from the processing equipment, it charges up rapidly leading to dielectric breakdown. The structure of the transistor, materials surrounding the transistors (e.g., insulation layers) and area of charge collection antennas determine how much current flows through the gate dielectric and the consequent damage that occurs to it. Examples are used to illustrate how this modeling infrastructure is being used to help design BEOL processes and integrations.

10:40am **PS+MS-ThM8 Computational Model for Ion Beam Extraction from a Pulsed Plasma Through a Grid*, S.-K. Nam*,** *V.M. Donnelly, D.J. Economou,* University of Houston

A computational model was developed to study the energy and directionality of an ion beam extracted from a pulsed plasma through a grid. First, a fluid model was used to obtain the space and time resolved profiles (at the periodic steady state) of the active glow (power ON) of the 13.56 MHz plasma. Then, the plasma evolution in the afterglow (power OFF) was followed with the fluid model. A positive DC bias voltage (acceleration voltage) was applied at a specific time in the afterglow to raise the plasma potential and expel positive ions out of the plasma and through the grounded extraction grid. The electric potential profiles found by the fluid model were in turn used as a boundary condition in a Particle-in Cell (PIC) simulation of ion flow through the holes of the grid. The output of the PIC simulation was the energy and angular distributions of the extracted ion beam. Fractional beam neutralization by ion contact with the metal grid was also determined. Beam directionality improved by extracting ions in the afterglow as the electron temperature dropped precipitously. A smaller diameter of the grid holes and a greater DC acceleration voltage also improved beam directionality. The energy distribution of the beam was very sharp (assuming ideal step accelerating voltage) except at higher pressures when ion-neutral collisions played a role. Work supported by NSF-NIRT and the Texas Advanced Technology Program.

11:00am **PS+MS-ThM9 CKnudsen - a Chemkin-based Collisionless Transport and Surface Reaction Simulator*, A.H. Labun,*** University of British Columbia - Okanagan, Canada

Reactive gas transport through a channel differs in the molecular flow (collisionless) regime from the flow in a fluid (collisional) regime. Chemical systems composed of gas and surface species and elementary reactions on the surface are simulated in the collisionless transport regime by CKnudsen, a new Chemkin code. Angular distributions for incident flux from all sources for each gas species are assembled at each point of the surface which encloses the volume. The system of simultaneous reaction rate equations is solved deterministically at each surface point. The reaction rates at each surface point together with the input angular flux distribution for each gas determine the angular distribution of reemitted flux for each gas. The use of the same Chemkin reaction formalism and subroutine libraries used by fluid codes facilitates multi-scale simulation and the validation of proposed reaction mechanisms in different regimes. As an example, Arora and Pollard's W CVD mechanism with 16 elementary surface reactions@footnote 1@ is converted into Chemkin format and evaluated at the equipment scale and then at the feature scale in submicron trenches and compared to experimental results. @FootnoteText@ @footnote 1@ R. Arora and R. Pollard, J. Electrochem. Soc. vol. 138, 1523-1537 (1991).

11:20am **PS+MS-ThM10 Simplified Model for the DC Planar Magnetron Discharge*, G. Buyle*,** *D. Depla, R. De Gryse,* Ghent University, Belgium

In order to investigate the DC planar magnetron discharge, we developed a simplified 2D model.@footnote 1@ This model differentiates itself from numerical models by analytically calculating the ionization caused by the high energy electrons, i.e. the electrons with energy above the ionization threshold. The model also takes into account that secondary electrons, which are emitted from the target due to ion bombardment, can be recaptured by the target.@footnote 2@ Here, the simplified model is extended such that the discharge current can be calculated. To achieve this extension, the Child-Langmuir law is applied and adapted to account for the specific magnetron discharge conditions. This way, a self-consistent model for the magnetron discharge is obtained. The extended simplified model allows investigating the influence of different external parameters on the magnetron discharge. The parameters considered are the magnetic field strength, the gas pressure, the secondary electron yield and the electron reflection coefficient. The latter two parameters are mainly determined by the target material. Special attention is given to the influence of these parameters on the current-voltage characteristic. Especially the considered target material properties seem to have a strong influence: increasing the secondary electron yield shifts the current-voltage characteristic to lower discharge voltages and increases its slope. Increasing the electron reflection coefficient leads to the same changes but their magnitude is larger. @FootnoteText@ @footnote 1@ G. Buyle et al., Vacuum 74 (3-4), 353-358, 2003.@footnote 2@ G. Buyle et al., J. Phys. D: Appl. Phys. 37, 1639-1647, 2004.

Plasma Science and Technology
Room 304 - Session PS-ThM

Plasma-Surface Interactions II

Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **PS-ThM1 Plasma-Based Techniques to Reduce/Remove Particle Contamination for Pelicleless EUV and Imprint Lithography*, D.N. Ruzic,*** *D.A. Alman, B.E. Jurczyk, H. Qiu, M.J. Neumann,* University of Illinois at Urbana-Champaign

Particle contamination on EUV surfaces during mask blank deposition, mask fabrication, patterned mask handling can create significant distortions and loss of reflectivity and must be avoided. Particles on the order of 10nm are problematic during MLM mirror fabrication, since the introduced defects disrupt the local Bragg planes. The most serious problem is the accumulation of particles on surfaces of patterned blanks during EUV light exposure, since >25nm particles will be printed without an out-of-focus pellicle. Particle contaminants are also a problem with direct imprint processes since defects are printed every time. Several plasma-based techniques are under investigation aiming to reduce particle contamination through the use of controlled electrostatic repulsion and expulsion of particles from surfaces. The preliminary experiment simulates the particle contamination of mirror samples by introducing external insulating nano-particles of 85% of particles. Particles are imaged with a high-resolution SEM and numerically counted using contrast information from the image histogram. The capabilities for extending this process to higher levels suitable for manufacturing will be discussed.

8:40am **PS-ThM2 Plasma-Surface Reactions at a Spinning Wall**, *P.F. Kurunczi, J. Guha,* ***V.M. Donnelly,*** University of Houston

We report a new method for studying plasma-wall interactions in near-real time. A cylindrical substrate is embedded in the reactor wall. This "spinning wall" is rotated up to 200,000 rpm, allowing the surface to be periodically exposed to the plasma (40% of the time) and then analyzed by a chopped molecular beam mass spectrometer (MS) in as little as 150μs after plasma exposure. Skimmers on the plasma side and analysis side of the spinning wall, and 3 stages of differential pumping allow a pressure of 10@super -10@ Torr in the MS with a 10 mTorr plasma. We have used this method to study oxygen plasma reactions on anodized Al. With the plasma off and substrate at rest, we observe a small signal at m/e = 32, due to O@sub 2@. When the substrate is rotated (plasma off) this signal increases slightly. When the substrate is at rest and the plasma is turned on, no increase in signal is observed. When the substrate is spun with the plasma on, however, a large increase in signal is observed with increasing rotation frequency. We interpret these observations as follows: O-atoms that impinge on the surface when it is in the plasma recombine over the ~0.7 to 30 ms period probed by changing the rotation frequency. We rule out O@sub 3@ (cracking in the MS ionizer to form O@sub 2@) from the absence of its parent ion. Likewise, we rule out shallow implantation of O@sub 2@@super +@ or O@super +@ as a cause of the O@sub 2@ signal; the dependence of the signal on rotation frequency did not change when grids were positively biased to reject positive ions. No desorbing O was observed; a signal at m/e=16 was entirely from the cracking of O@sub

2@. Finally, no ions were observed with the MS ionizer off. Modeling of O@sub 2@ signal vs. rotation frequency indicates a range of recombination rate constants, suggesting a range of O-binding energies on anodized Al. Supported by ACS-PRF. @FootnoteText@ P.F. Kurunczi - Present affiliation: Varian Semiconductor Equipment, Gloucester, MA 01930.

9:00am **PS-ThM3 Innovative Strategy to Improve the Stability of Plasma Processes*, R. Ramos*,** *G. Cunge, B. Pelissier, O. Joubert,* CNRS/LTM, France

Plasma process drifts associated with changes in the reactor wall conditions have become a major issue in silicon etching processes used in integrated circuit fabrication. The solution today to achieve good wafer-to-wafer repeatability is the dry-cleaning of the chamber in fluorine-based plasma between each wafer. However, this procedure leaves AlF residues on the Al@sub 2@O@sub 3@ reactor walls. This leads to several issues including flake off of AlF@sub x@ particles on the wafer and process drifts - due both to the progressive growth of AlF material and to the release of F atoms from the chamber walls during the etching process. For all these reasons, we are introducing here a new strategy to improve the stability of plasma processes. Before the etching process, a thin carbon-rich layer is deposited on the reactor walls by a short plasma step. After silicon gate etching, the SiOCl layer formed on the carbon layer is cleared with an appropriate plasma chemistry and the carbon layer removed by an O@sub 2@ plasma, thus resetting the reactor walls to their initial state. Using this strategy the process is perfectly reproducible since it always starts under the same carbon-rich chamber walls conditions. At the same time, issues associated with AlF deposits are prevented because chamber walls are protected from aggressive fluorine-based cleaning plasma. X-ray Photoelectron Spectroscopy analysis of the reactor wall surfaces is used to show feasibility and efficiency of this technique in an industrial context. Then performance of state-of-the-art silicon gate etching process in carbon-coated chamber and in traditionally seasoned chamber are compared in terms of feature profile, etch rate and selectivity toward gate oxide. Correlation with time-resolved broad-band UV absorption spectroscopy analysis of plasma gaseous phase suggests promising future of this strategy for metal gate etching.

9:20am **PS-ThM4 Interactions of Plasmas with Model Polymers for Advanced Photoresists*, S. Engelmann*,** *X. Hua, T. Kwon, R. Phaneuf, G.S. Oehrlein,* University of Maryland*; Y.C. Bae,* Rohm and Haas Electronic Materials*; D.B. Graves, E. Paragon,* University of California, Berkeley*; E.A. Hudson,* Lam Research Corp.*; P. Lazzeri, E. Iacob, M. Anderle,* ITC-Irst, Italy

Plasma-based pattern transfer of lithographically produced nanoscale patterns in advanced resist materials is often accompanied by resist surface roughening and line edge roughening. The properties of the organic imaging materials or fully formulated resist systems as well as the reactive particle fluxes and microscopic parameters of the plasma processing environment contribute to these changes. In this collaboration, we seek to establish a basic understanding of these phenomena by investigating the interaction of a number of carefully selected model polymers like those used in advanced photoresist materials, along with fully formulated 193nm and 248 nm photoresist systems, with well characterized plasmas. We have systematically studied the evolution of surface roughening and surface composition in these systems using H@sub 2@, O@sub 2@, C@sub 4@F@sub 8@/Ar and Ar discharges produced in an inductively coupled plasma (ICP) reactor. Etching rate, surface composition and chemical structure was evaluated using Ellipsometry, Atomic Force Microscopy, Fourier-Transform Infrared Spectroscopy, Static Time-of-Flight Secondary Ion Mass Spectrometry and X-Ray Photoelectron Spectroscopy. The exposed compounds showed different chemical evolutions for various plasma exposures. We will discuss these differences with regard to the chemical structure of the different monomers used in the model compounds.

9:40am **PS-ThM5 Decomposition Mechanisms of 193 nm Photoresist under Ar+ and Radical Bombardment*, E. Pargon*,** *D. Nest, D.B. Graves,* University of California at Berkeley*; G.S. Oehrlien, S. Engelmann, X. Hua,* University of Maryland*; Y.C. Bae,* Rohm and Haas Electronic Materials, L.L.C.*; E.A. Hudson,* Lam Research Corporation

193 nm methacrylate-based photoresists are known for their limited etch resistance and enhanced surface roughening compared to 248 nm photoresist. In this study, we examine the decomposition mechanisms of three 193 nm methacrylate-based photoresist formulations in a vacuum beam experiment. The vacuum beam system allows separate control of incident ionic and neutral radical species, more controlled exposure protocols and direct detection of etch products. The results obtained in the beam experiment are compared to complementary and analogous measurements made in a plasma etch environment. Photoresist samples are exposed to an Ar+ ion beam (100 eV - 1000 eV) and various radical beams. The species leaving the surface are detected in an in-situ threshold ionization quadrupole mass spectrometer. Film thickness and mass change are monitored during and after beam exposure. FTIR is used in transmission mode to detect changes in film structure after beam exposure. The primary volatile species leaving the room temperature photoresist surface during Ar+ ion bombardment are CO and H2O, with significant quantities of CO2 and C2H2 also detected. Volatile species initially leave the surface at a higher rate, and the initial etch rate is significantly higher than the average etch rate. FTIR measurements after beam exposure show that the most significant changes occur in the CH2 and CH3 stretching modes (3000 cm-1), although other changes in the carbonyl region (1700 cm-1) are observed as well. We report the effects of beam exposure on surface roughness as measured by ex-situ AFM. The impact of surface temperature and various radical fluxes (H, N and O) on decomposition rate and product distribution will also be reported.

10:00am **PS-ThM6 Investigation of Feature Surface Roughening using Plasma Beams*, Y. Yin*,** *H.H. Sawin,* MIT

Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. The primary cause of sidewall roughening is the templating of mask roughness into the underlying film. Specifically, the inherent roughening of photoresist provides the mask for templating effect. To fully understand the sidewall roughness evolution, it is critical to characterize the inherent roughening of photoresist as well as other materials, such as porous low-k film. A polymerization-induced micromasking mechanism was proposed to explain the surface roughening of porous low-k films. Porous structure in the substrate plays a critical role in the film roughening evolution. This effect can be understood using the concept of pore filling with polymeric deposition that etches more slowly under fluorocarbon plasma exposure. Later on, the polymer forms micromasks that induce roughening. Although scaled with the ion bombardment energy, the roughness level of porous low-k film etched in C2F6 plasma is mainly related to the film thickness removed; no similar trend was observed on non-porous OSG films under same etching conditions. Fluorocarbon plasmas with different polymerization capabilities such as 20% C4F8/ 80% Ar, were used to explore the polymerization effects. Additionally, the correlation between polymer deposition and porosity/pore size distribution of low-k films was investigated. The roughening of photoresist blank films can also be explained based upon the mechanism proposed above. It was found that photoresist roughening was influenced by etching chemistries and some other factors. In particular, the inhomogeneity introduced during blank film development process formed some equivalent "pores" at near surface region. These "pores" had significant impact on the roughness evolution during etching in fluorocarbon plasmas.

10:20am **PS-ThM7 3-Dimensional Feature Scale Profile Simulation of Sidewall Roughening During Plasma Etching*, H. Kawai*,** *B. Bai, H.H. Sawin,* Massachusetts Institute of Technology

Sidewall roughness or Line Edge Roughening (LER) is becoming an ever more significant issue as the line width of integrated circuits features shrink and the size of width variation caused by LER becomes comparable to the minimum feature dimension. Since roughening is inherently a three dimensional phenomenon, we have developed a 3-dimensional feature scale profile simulator to simulate the surface and sidewall roughening during the etching process of polysilicon and silicon dioxide. The simulator uses a dynamic Monte Carlo simulation to model the surface kinetics. The simulation domain is discretized into array of cubic cells with the side of 2.5 nm. The local surface conformation is determined by fitting the local region of the surface cells with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Using the angular dependence of physical sputtering with a highest etching yield at 60 degrees off-normal incident angle, the initially smooth polysilicon surface is roughened with facets of approximately 60 degrees after the surface is sputter-etched at normal incident angle. Non-planar surfaces are etched and evolve to the same surface roughness as was found for the initially planar surface. However, using the angular dependence of ion (chlorine) etching yields where yield decreases monotonically with off-normal angle, an initially smooth polysilicon surface tends to stay smooth after it is etched at normal incident angle. The surface with small, shallow angle initial roughness also smoothes when it is etched at glancing incident angle, but the surface with large, steep features forms striations after it is etched due to the scattering of ions. Templating, also known as top LER, the most common mechanism of LER caused by mask edge roughening, has also been modeled. This LER is characterized by the transference of the mask spatial frequencies with reduced amplitude with distance from the mask.

10:40am **PS-ThM8 Surface Modification of Photoresists in Electron Beam-Generated Plasma*, B. Orf,*** *G.S. Oehrlein,* University of Maryland at College Park*; D. Leonhardt, S.G. Walton,* US Naval Research Laboratory

An electron beam (e-beam) generated plasma system has been used to study the factors that contribute to plasma-induced surface modifications of UV photoresists. Due to the low electron temperature of e-beam generated plasmas, minimum ion energies are much lower than in RF excited plasma discharges, and can be more accurately controlled in the low energy regime. Thus surface modifications such as roughening, compositional changes, and bond rearrangements (i.e. cross-linking, graphitization) can be studied systemically with respect to the ion energy. In this work we have examined the interaction of Ar and Ar/fluorine plasmas with commercial 193 nm and 248 nm photoresists. Following plasma exposure, the photoresist films were characterized ex situ by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), contact angle measurements and ellipsometry. Ion energy and exposure time were carefully selected to establish the role of ion bombardment in the surface modification, and determining the threshold energies for photoresist damage versus etching. Additionally, the effect of surface relaxation time was investigated by modulating the e-beam generated plasma, to understand how long-lived radicals and the organic material react during the plasma afterglow. The observed differences in behavior of the 193 nm and 248 nm photoresists will be discussed in terms of compositional and structural differences of the materials.

11:00am **PS-ThM9 Nanoscale Plasma Processing of Substrates Using Moving Patterned Shutter*, X. Hua,*** *G.S. Oehrlein,* University of Maryland*; P. Lazzeri, M. Anderle,* ITC-irst, Italy

Future nanoscale device fabrication may require the ability to add or remove controllably layers of several nanometers using plasma processes. For such processes, the total length of the substrate-plasma interaction time decreases to a few seconds and less. For short plasma-substrate interaction times, transient plasma effects, e.g. electrical matching and plasma stabilization, plasma-wall interactions, etc., play a more important role than for longer plasma processes, and reduce our ability to control the plasma induced modification of a substrate. In this presentation, we describe the concept of a moving shutter containing slits in close contact with a substrate to control the interaction time of well-established gas discharges with the substrate for nanoscale layer/nanostructure processing. Both substrate and shutter are located on the RF powered electrode and can be biased relative to the plasma. Once the plasma density, discharge chemistry, and the electrode bias voltage are fully established, the shutter with slits begins to move at a controlled speed across the initially covered substrate and exposes the substrate for the desired interaction time to the plasma. We will show that this technique enables precise nanoscale layer etching or deposition on both blanket and patterned substrates employing gas discharges. Applications of this approach to nanoscale plasma processing of ultra low k materials and surface modifications of advanced photoresist materials are reviewed.

11:20am **PS-ThM10 Investigation of the Etching Characteristics of SrTiO@sub 3@ Films in Halogenated High-Density Plasmas*, L. Stafford*[1]*,*** *O. Langlois,* Universite de Montreal, Canada*; M. Gaidi,* INRS-Energie, Materiaux et Telecommunications, Canada*; J. Margot,* Universite de Montreal, Canada*; M. Chaker,* INRS-Energie, Materiaux et Telecommunications, Canada*; J. Saussac,* Universite de Montreal, Canada

SrTiO@sub 3@ (STO) films have recently received much attention because of their potential applications into waveguides for optical integrated systems. Up till now, relevant issues related to the development of an efficient patterning process for STO remain however to be solved. This is vital since the performances of the device critically depend upon the STO etching characteristics, particularly upon the roughness of the etched profiles. In this context, we investigate in this work the etching characteristics of STO films using a low-pressure high-density plasma operated in halogenated gas mixtures. We found that the addition of Cl@sub 2@ and SF@sub 6@ to the Ar plasma significantly reduces the etch rate. A correlation between the etch rate data and the plasma characteristics obtained from Langmuir probes and actinometry, indicates that this decrease results in part from the lower positive ion density in Ar/Cl@sub 2@ and Ar/SF@sub 6@ plasmas. Using a recently developed surface reaction model for ion-assisted chemical etching,@footnote 1@ we demonstrate that in both Ar/Cl@sub 2@ and Ar/SF@sub 6@ plasmas, (i) the etch rate is ion-flux limited (i.e. independent of the reactive neutral density) and that (ii) chlorine and fluorine reactive neutral species act as inhibitors in the etching process of STO. A characterization of the post-etched surface by X-Ray Photoelectron Spectroscopy (XRPS) and Secondary Ion Mass Spectrometry (SIMS) measurements indicates that inhibition results from the formation of a thin SrCl@sub x@ or SrF@sub x@ layer, which impedes the formation and/or the desorption of TiCl@sub x@ or TiF@sub x@ volatile products. Finally, based on XRPS and SIMS measurements, we propose a two-layer model for the representation of the surface in the course of etching. @FootnoteText@ @footnote 1@ L. Stafford, J. Margot, M. Chaker, & S.J. Pearton, "Energy dependence of ion-assisted chemical etch rates in reactive plasmas", submitted to Appl. Phys. Lett. 21/12/2004.

11:40am **PS-ThM11 A Numerical Model for Profile Anomalies Caused by Surface Charging during Etching and Overetching of Polysilicon*, Y. Osano,*** *K. Ono,* Kyoto University, Japan

The precise control of etched profiles in gate etch processes is one of the most important issues. However, the mechanism of etching processes is not fully understood; in particular, the particle transport and reaction processes in microstructures are considerably difficult to be understood, owing to a number of physical and chemical effects. Among these effects, the surface charging on insulating masks during etching causes the deflection of ion and electron trajectories in microstructures. Moreover, the charging on electrically floating poly-Si on SiO@sub 2@ films during overetching step causes a significant deflection of ion trajectories in microstructures. It is generally appreciated that the deflection of ion trajectories leads to the nonuniformity of ion fluxes onto the feature surfaces, which in turn results in profile anomalies such as bowing, microtrenching, and notching. In this paper, we present a phenomenological, pseudo atomic scale model to simulate the feature profile evolution of Si etching in Cl@sub 2@. The model incorporates the surface charging in microstructures, to investigate its influence on the profile evolution. The particle transport of Cl@super +@ ions, Cl neutrals, and electrons in microstructures onto etched substrates is analyzed by the Monte Carlo calculation. The model gives the electrostatic potential distribution, along with the differential charging that occurs on insulating masks, electrically floating Si, and SiO@sub 2@ films. The flux of ions and electrons onto feature surfaces is self-consistently analyzed by taking into account their deflection due to Coulomb interaction with charged feature surfaces. The feature profile evolution is presented by the cell removal method. The numerical simulation is performed with different incident ion energies and pattern widths. Emphasis is placed on the mechanism for the formation of microtrenching and notching, which are generally considered to be mainly caused by the surface charging.

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[1] **PSTD Coburn-Winters Student Award Finalist**

Plasma Science and Technology
Room 302 - Session PS+TF-ThA

Emerging Plasma Applications

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **PS+TF-ThA1 Emerging Plasma Deposition Applications***, **D.P. Monaghan**,* Gencoa, UK **INVITED**

Vacuum plasma deposition has been the mainstay of the thin film industry since its inception. In particular magnetron sputter based processes have come to the forefront due to the inherent stability and scalability of the technique. However, the method has to constantly re-invent itself in order to provide better solution for the ever-changing world of micro-electronics and consumer products. New generations of products are also being created that rely partly or completely on new sputter based processes. This in turn can require radical changes to the usual production methods. The presentation will highlight the state-of-the art in sputter technology and in particular a number of areas that will drive further market expansion and technical advancement in the field. Some examples will include thin film batteries where virtually every feature relies upon sputtered layers of a low or high tech. nature. Due to the miniature and highly efficient nature of the product, it opens up the possibility of providing "power" to many new product classes and new devices. Thin film solar cells that have the ability to create efficient conversion of energy via a low cost and lightweight structure may lead to a reduction of societies dependence upon fossil fuels. The introduction of vertical magnetic recording comes ever closer if longitudinal recording is limited to <200 Gbit/in2. Vertical recording can potentially achieve terabyte recording density, but places much higher demands on the process equipment and magnetron source technology. Another high growth area is display technology. The emergence of high definition large area LCD displays puts a corresponding demand upon the digital video disk storage capacity. New disk formats such have Blu-ray have been shown to offer up to 3x the storage capacity. In addition the possibility of a high and low video formats on a single disk means the creation of two separate recording media in a single production process.

2:40pm **PS+TF-ThA3 Investigating the Plasma-Propellant Interaction through Experimental Modeling***, **R. Valliere**, R. Blumenthal,* Auburn University

There has been a significant interest in the use of plasmas to ignite propellants in large bore artillery. A short, reproducible ignition delay and a reduced temperature dependence are the most important advantages of plasma ignition over conventional ignition. Using the experimental modeling method, pioneered by Winters and Coburn,@footnote 1@ the erosion rates of sprayed-on films of RDX and HMX have been investigated in inert and reactive plasmas, as a function of sample bias in order to isolate the ion and electron bombardment and chemical effects on the erosion rate. No significant erosion rate was observed in argon plasmas with zero or positive bias, indicating that erosion by electron bombardment alone is not significant. Under ion bombardment conditions, large negative bias, only a slow erosion rate (presumably due to sputtering) was observed. Erosion in hydrogen plasmas is quite different. The minimum erosion rate, observed at positive and zero sample biases, was ~100x the maximum rate observed in negative-biased argon plasmas. Under negative bias the erosion rate increased as a much as 20-fold, depending on a combination of ion current and sample bias. All observed erosion rates obey pseudo-first order kinetics. The fact that the erosion rates in the hydrogen plasmas are all much greater than the rates of the argon plasmas, even at large negative bias, indicates a strong chemical component to the erosion process. The bias and current dependence of the erosion rate in hydrogen plasmas indicate a synergistic effect between ions and reactive neutrals. The kinetics of erosion for the individual species and the synergistic effects between them will be presented. @FootnoteText@ @footnote 1@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

3:00pm **PS+TF-ThA4 PECVD of SiO@sub 2@ Thin Film from Electron-Beam Generated Plasmas***, **D. Leonhardt**, S.G. Walton,* US Naval Research Laboratory

The deposition of thin films of SiO@sub 2@ is an integral part of flexible displays/electronics, medical implant bio-functionalization, as well as a robust barrier layer ideal for space applications. In all of these applications, the SiO@sub 2@ layer must be uniform and defect free over large areas. Typical plasma-based deposition technologies that are presently used have limitations in both the quality of material being deposited and the uniformity over large (square meter) areas. NRL has used electron beam-generated plasmas to produce a variety of SiO@sub x@ films, with the focus on PECVD processes for temperature sensitive substrates that are scalable to large areas. Mixtures of TEOS or HMDSO with Ar/O@sub 2@ based plasmas were used to grow films in modulated electron beam generated plasmas. The inherent low electron temperature of these plasmas results in low plasma fields and potentials, which in turn provide low energy (< 3 eV) ions to the substrate. The resultant film electrical, optical and chemical properties with respect to gas mixtures, substrate temperature and ion energy will be presented. The low ion energies were critical in producing films with lower defect densities than typical SiO@sub 2@ deposition processes. Using the ion energy as an additional process control 'knob' the film composition ranged from stoichiometric SiO@sub 2@ to heavily hydrolyzed. Fluxes to the substrate determined by mass spectrometry measurements will be correlated to these process variables and final film composition. Along with a highly tunable PECVD process, these plasmas offer tremendous scaling and uniformity capabilities that will also be discussed.

3:20pm **PS+TF-ThA5 Nanoparticles and Nanocoatings from Plasmas: Old Problems with a New Twist***, **K.P. Giapis**,* California Institute of Technology **INVITED**

The formation of particles in processing plasmas has generally been related to contamination and lower yields and is considered undesirable. However, nanometer-size particles can have unusual properties, very different from those of bulk materials, which makes them attractive for nanotechnology applications. We have explored the formation of Si nanoparticles in continuous-flow atmospheric-pressure dc microdischarges confined in capillary tubes. The intensity and size of these discharges permits the rapid decomposition of silane, leading to nucleation and growth of 1-3 nm Si particles, whose growth is abruptly terminated as they exit the microreactor. Narrow size distributions are obtained as inferred from classification and imaging. Particles of both charge polarities are detected with similar size distribution but 2X more positively charged particles. As-grown Si particles luminesce in the blue (420nm) with a quantum efficiency of 30% and may find applications in imaging and Si-based optoelectronics. The microdischarge synthesis route is generic to any gas-phase precursor and has been also used to grow Ge and Fe nanoparticles of 1-3 nm in size in benchtop setups. Nanowires and nanotubes are promising as nanoprobes, provided they can be coated with insulating materials followed up by tip end exposure and functionalization. We have used inductively-coupled plasmas to deposit conformal fluorocarbon coatings of a few nm thickness on carbon nanotubes. The coatings provide good insulation while they improve the rigidity of the nanotubes for surface imaging. We will present results from probe immersion experiments in Hg and water. Plasmas provide a versatile way to deposit a wide variety of extremely thin coatings to enable passivation, isolation, or functionalization at the nanoscale.

4:00pm **PS+TF-ThA7 Effect of Substrate Material on Properties of TiN Films Deposited in the Hybrid Plasma Reactor***, **L. Bardos**, H. Barankova, L.-E. Gustavsson,* Uppsala University, Sweden

Parameters of TiN films deposited in the hybrid hollow cathode and microwave ECR plasma reactor can be strongly affected by the substrate material. Differences have been found between films grown on Si substrates and steel substrates, as well as between steel substrates from martensite and austenite steels. Temperature measurements by simple probes made from different materials with surfaces covered by wafers from Si or from steel confirmed substantial differences depending on individual materials. These differences can be explained by material-dependent absorptions of the microwave power as well as by enhanced particle bombardment of ferromagnetic substrates connected with deformation of the magnetic field in the hybrid plasma reactor. The effect of surface bombardment has been confirmed by voltage current measurements using electrically biased probes. The results correspond well with properties of the obtained TiN films. Observed effects could be of more general importance, e.g. for microwave ECR plasmas, magnetron sputtering as well as for most magnetized plasma systems.

4:20pm **PS+TF-ThA8 Synthesis of Aligned Carbon Nanotubes by RF-Plasma-Assisted DC Plasma Chemical Vapor Deposition***, **Y. Hayashi**, T. Fukumura,* Kyoto Institute of Technology, Japan*; R. Utsunomiya,* Nissin Electric Co. Ltd., Japan

Aligned carbon nanotubes (CNTs) grown on a substrate are expected to be applied to the electron emitters of a field emission display. Plasma-enhanced chemical vapor deposition (plasma CVD) enables highly aligned growth of multi-walled CNTs by drawing them toward plasma in the sheath electric field.@footnote 1@ However the problem of aligned CNT growth by plasma CVD is large-area growth. We have developed a new method of large-area growth of CNTs under stable DC plasma sustainment without arcing by the assistance of RF plasma. Plates of RF electrode, a grounded electrode, and DC cathode were placed parallel in this order in a vacuum chamber. The grounded electrode was gridded so as to pass a part of the RF generated plasma into the space of DC discharge. Iron substrates were placed on the cathode electrode. 13.56 MHz RF power of 500 W was induced to the RF electrode and negative bias of 325 V was induced to the cathode electrode. 20 % methane diluted in hydrogen was introduced into the chamber with the operating pressure of 1000 Pa during the growth of CNTs. Well-aligned carbon fibers were observed by scanning electron microscopy and about 50 concentric layers of graphite with hollows were observed by transmission electron microscopy. These results confirm that CNTs can be synthesized by this method. DC discharge current was 0.7 A at the discharge voltage of 325 V under the assistance of 500 W RF-plasma, while it was 0.57 A without RF-plasma. The decrease of discharge impedance caused the stable sustainment of DC glow discharge without arcing. It is concluded that the large-area growth of well-aligned CNTs under the stable sustainment of DC glow discharge can be carried out by RF-Plasma-Assisted DC Plasma CVD. @FootnoteText@ @footnote 1@Y. Hayashi, T. Negishi and S. Nishino, J. Vac. Sci. Technol. A19, 1796(2001).

4:40pm **PS+TF-ThA9 In Situ Oxidation and Plasma Studies for Magnetic Tunnel Junctions: The Mechanism of Plasma Oxidation of Ultra-Thin Aluminum Films Unraveled***, **M.C.M. Van De Sanden,*** Eindhoven University of Technology, The Netherlands*; K. Knechten,* Oce Technology, The Netherlands*; B. Koopmans, H.J.M. Swagten, W.J.M. de Jonge,* Eindhoven University of Technology, The Netherlands

Plasma oxidation of thin aluminum films is a commonly used technique to form thin aluminum oxide barriers for application in magnetic tunnel junctions (typically 1 nm). In this technique a glow discharge in oxygen (P = 5-12 W, p = 5-40 Pa) is used to oxidize ultra thin sputtered aluminum films. In comparison with thermal oxidation the process is faster and provides high values of tunneling magnetoresistance (TMR) but at the cost of higher resistance-area products (RxA). However, whereas thermal oxidation of thin aluminum films is well understood in terms of the original model of Cabrera, where the oxidation rate is limited by field-assisted thermal 'hops' of aluminum ions into the oxide, the detailed mechanism of plasma oxidation of thin aluminum films is still unknown. To unravel the mechanism in situ measurements of the oxidation rate and plasma parameters such as the ion and oxygen density are performed. The oxidation rate is determined from single wavelength ellipsometry. From these measurements we have concluded that not one single particle in the plasma is responsible for the increase in oxidation rate observed. A clear correlation of the oxidation rate with the ion flux towards the sample is observed. In addition the oxidation rate is also correlated with the atomic oxygen density in the gas. These results can be explained within a modified Cabrera model of oxidation in which the oxidation temperature is locally enhanced due to the thermal spike of an impinging ion. Additionally, due to the presence of atomic oxygen in the plasma, the field over the oxide during oxidation is enhanced by the increased adsorption of atomic oxygen on the oxide surface. Including both effects in an adjusted equation for the oxidation rate provides a good agreement between model and experiments. The model provides new insights into plasma based oxidation of ultra thin films and offers oppertunities to further control the quality of the tunnel barrier.

5:00pm **PS+TF-ThA10 High Density Plasma Processing of Si Nanocrystal Embedded SiO@sub x@ Thin Films***, **P.C. Joshi,*** SHARP Labs of America, Inc., US*; T.K. Li, W. Gao, Y. Ono, A.T. Voutsas, J.W. Hartzell, S.T. Hsu,* SHARP Labs of America, Inc.

The optical properties of Si nanocrystals are of interest for efficient and low cost integrated optoelectronic applications. The fabrication of novel optoelectronic devices, exploiting the unique optical properties of Si nanocrystals, requires thin films with high PL/EL quantum efficiency. One approach that is being actively pursued for optoelectronic devices is the fabrication of Si nanocrystal embedded SiO@sub x@ thin films. The development of stable and reliable optical devices requires thin films with high concentration and uniform distribution of Si nanocrystals with controlled particle size. In this paper, we report on the high-density plasma processing of Si nanocrystal embedded SiO@sub x@ thin films. The high-density plasma technique is characterized by low plasma potential, high plasma density, and independent control of plasma energy and density; which provide unique process possibilities and control. The high plasma concentration and low plasma potential of the HDP process are attractive for the generation of Si nanocrystals while minimizing the plasma induced bulk and interfacial damage. We have been successful in controlling the optical properties SiO@sub x@ thin films and the wavelength of the emitted PL signal over a wide range exploiting the unique characteristics of the high-density PECVD technique. The present paper describes a correlation between the optical properties and the PL characteristics of the SiO@sub x@ thin films deposited in the temperature range of 25-300 °C. The high-density plasma deposited SiO@sub x@ films have shown PL signal even in the as-deposited state while subsequent annealing (900-1100 °C) has resulted in significant enhancement of the PL intensity. The present results demonstrate the potential of the high-density PECVD technique for the low temperature processing of the Si nanocrystal embedded SiO@sub x@ thin films with controlled physical and optical characteristics for novel optoelectronic applications.

Plasma Science and Technology
Room 304 - Session PS-ThA

Plasma Sources and Equipment

Moderator: G.F. Franz, Munich University of Applied Sciences, Germany

2:00pm **PS-ThA1 Characteristics of Large-diameter Plasma using a Radial Line Slot Antenna***, **C. Tian**, T. Nozawa, K. Ishibasi, H. Kameyama, T. Morimoto,* Tokyo Electron LTD., Japan

A radial line slot antenna (RLSA) for surface-wave-plasma at 2.45GHz is a promising candidate with respect to increased process requirements for the large-diameter plasma as well as the gas dissociation control and free plasma damage. Characteristics of such a kind of plasma have been studied by both direct plasma probe measurements and numerical simulations. The discharge chamber is 40 cm in diameter and 30 cm in depth with a quartz glass window 3 cm thick on the top. A custom inductively coupled plasma (ICP) is also evaluated for comparison by replacing the RLSA with an RF coil mounted on the top window. Some unique characteristics of RLSA has been found by both radial and vertical direction plasma measurements, which are: (1) the electron temperature of RLSA is about 0.9eV-1.2eV low under the various power input and gas pressure conditions, half as many as the ICPs; (2) the main plasma generation area of RLSA is limited in the plasma surface just below the quartz glass window, while the ICP involve a much wider range; (3) the electron energy distribution functions (EEDFs) of RLSA plasma show few high energy electrons existing in the plasma diffusion area as compare to the ICPs. Numerical simulations are implemented to reveal the more essential difference in plasma generation between the RLSA and the ICP, where the superiority of RLSA plasma has been confirmed. The critical uniformity of the radial plasma distribution has been evaluated by the view of RLSA optimization. Optimal design of the slot pattern and the top glass window shape are effective in keeping the high plasma uniformity robustly from various processing conditions. Numerical analysis of microwave propagation helps to achieve the RLSA optimal design. The features of high plasma uniformity and low electron temperature lead to free plasma damage in our associated etching process.

2:20pm **PS-ThA2 Application of the Shaped Electrode Technique to a Large Area Rectangular Capacitively-Coupled Plasma Reactor to Suppress Standing Wave Non-Uniformity***, **L. Sansonnens,*** Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; C. Ellert, A. Buechel,* UNAXIS-Balzers AG, Liechtenstein*; H. Schmidt, A.A. Howling, C. Hollenstein,* EPFL, Switzerland

The use of VHF (very high frequency) instead of the standard 13.56 MHz excitation frequency in capacitively-coupled plasma reactors has been shown to be a promising technique for plasma-enhanced chemical vapor deposition of thin films such as amorphous or microcrystalline silicon used for the production of photovoltaic solar cells or thin film transistors for flat screens. In particular, the use of VHF has been shown to increase the deposition rate and to reduce the sheath voltage and maximum ion energy bombardment at constant plasma power. Both effects favor deposition at higher rates without degrading the thin film electronic properties. However, these advantages have generally been demonstrated in small area plasma reactors, and it has been shown that electromagnetic standing wave effects becomes the main source of non-uniformity limiting the use of VHF in large area reactors exceeding 1 m@super 2@ required for industrial applications. Recently, it has been proposed to use a shaped electrode (together with a thin dielectric plate in order to confine the plasma in a constant interelectrode gap) in place of the conventional flat electrode in order to suppress the standing wave non-uniformity. In this work, the application of the shaped electrode technique for standing wave suppression in a large area rectangular industrial reactor (substrate area: 1.1 m x 1.25 m) will be presented. In particular, film thickness uniformities for amorphous silicon deposited with and without shaped electrode at an excitation frequency of 41 MHz will be compared, and some of the implementation difficulties of the shaped electrode technique for industrial processes will be discussed.

2:40pm **PS-ThA3 Characteristics of Internal Linear Inductively Coupled Plasma and Its Etching Properties for Flat Panel Display Applications*, G.Y. Yeom*,** *K.N. Kim, C.K. Oh,* Sungkyunkwan University, Korea **INVITED**

The increase of substrate size and the requirement of high rate processing for both microelectronics and flat panel display industry require large-area high density plasma sources. Among the various high density plasma sources, inductively coupled plasma sources are preferred due to its simple physics and scalability. However, conventional spiral-type external inductively coupled plasma sources can not be easily applied to the flat panel display processing due to the standing wave effect, increased capacitive coupling, etc. In this study, characteristics of an internal linear inductively plasma source was investigated as a possible high density plasma source for the application to flat panel display processing larger than 7th generation of TFT-LCD substrates. By varying the arrangements of the antenna arrays, the uniformity of the plasma has changed significantly, and, by optimizing the antenna arrangement, the plasma uniformity of 4% with the plasma density higher than 2x10@super11@ /cm@super3@ could be obtained on the substrate. Electrical characteristics of the plasma source measured by an impedance analyzer showed the low impedance and high power transfer efficiency for the optimized antenna arrangement.

3:20pm **PS-ThA5 Investigation of Frequency and Magnetic Field Effect on Single and Multiple Frequencies Capacitively Coupled Plasma Reactors*, T. Panagopoulos*,** *A.M. Paterson, J.P. Holland,* Applied Materials Inc.

The effect of driving frequency and magnetic field has been investigated for a 300 mm MERIE reactor for an argon discharge using the HPEM hybrid-fluid computational model. The driving frequency varied from 2 MHz up to 200 MHz for either single or multiple frequency operation, while the magnetic field range was 0 to 225 G. Pressure was maintained low, at 30 mTorr, where the magnetic field has the most dominant effect and the power was held constant at 400 W. As the magnetic field increases the dc bias becomes less negative and the difference between plasma potential and dc bias is reduced and becomes minimal at high values of magnetic field. For low driving frequencies, up to 20 MHz, the dc bias increases (becomes more negative) with a small increase in magnetic field (40 MHz), the dc bias becomes less negative monotonically with the B field intensity. For high magnetic field (~170 G), the frequency effect on dc bias is rather weak. The electron temperature at reactor centerline decreases with increasing frequency and increasing magnetic field intensity, while the argon metastable and argon density follow opposite trends with one another at the same location. The plasma density increases with the frequency and magnetic field, while the argon metastable density peaks at low B field initially and then decreases at higher B field. The plasma potential decreases both with increasing magnetic field and driving frequency. At higher frequencies (>20 MHz) and values of magnetic field greater than 50 G, the plasma potential increases with the magnetic field and saturates at values around 200 G. Experimental results using langmuir and V-I probes confirm the trends observed in the simulation study.

3:40pm **PS-ThA6 Independent Control of Backscattering Energy and Sputter Rate in a VHF-DC Superimposed Magnetron Source*, H. Toyoda*,** *Y. Sakashita, Y. Takagi, K. Sasaki, J. Gao, T. Kato, S. Iwata, S. Tsunashima, H. Sugai,* Nagoya University, Japan

Recent application of magnetron plasma to nano-scale thin film deposition requires damage-free atomic-scale flat surfaces of the deposited film. In general, surface qualities of sputter deposited films are influenced by the incidence of particles with high kinetic energies. Thus, control of energetic ions and neutrals impinging on substrate is an important issue, in order to clarify a correlation between energetic particles and film qualities. In the magnetron discharge in argon gas, a significant amount of energetic Ar atoms is backscattered from the target surface and incident on the substrate. The backscattering energy can be reduced by lowering the target voltage, but it results in a decrease in the sputter deposition rate. In this study, we present independent control of the backscattering energy and the sputter deposition rate by superimposing VHF and DC voltage to the target. Discharge characteristic and sputter deposition rate are investigated by a Langmuir probe, a quadrupole mass spectrometer (QMS) with an energy analyzer and a quartz crystal microbalance. From the QMS measurement of energetic Ar ions, a decrease in the energy of backscattered Ar atoms is inferred. It is confirmed that the sputter deposition rate of the VHF-DC superimposed magnetron discharge at lower target DC voltage (~100 V) is almost comparable to that of the conventional DC magnetron discharge at higher target voltages (>400 V).

4:00pm **PS-ThA7 Extraction of a Directional, Nearly Mono-energetic Ion Beam Using an Inductively Coupled Pulsed Plasma with an Internal Coil*, L. Xu*,** *D.J. Economou, V.M. Donnelly, P. Ruchhoeft,* University of Houston

Ion beams with narrow energy and angular distributions are important for large-area sub-10 nm feature etching and deposition. In this work, a 13.56 MHz pulsed (typically 100µs ON/100µs OFF) inductively coupled plasma reactor with a two-turn nickel coil immersed in the plasma was developed to generate a nearly mono-energetic, directional ion beam. This beam may be used for etching (Ar@super +@ ions on silicon exposed to chlorine) or deposition (low energy Ni@super +@ ions on silicon). The plasma chamber was separated from the differentially pumped processing chamber by an ion drift region. A three-grid ion energy analyzer located in the processing chamber, 75 cm from the ion source, was employed to measure the ion energy distribution (IED) and ion current density. A positive voltage pulse synchronized with the power-OFF (afterglow) period of the pulsed discharge was applied to an extraction ring electrode surrounding the plasma, raising the plasma potential (V@sub p@) and "pushing" positive ions out of the plasma through a grounded grid. With 100 V applied to the extraction ring electrode during the afterglow, the energy of the extracted ion beam peaked at 100.5 eV, and the FWHM of the IED was 3.0 eV. The corresponding ion current (measured by the analyzer with 1 degree acceptance angle) was 20 times higher than the ion current extracted during the power-ON (active glow, no acceleration voltage) period. This is because ions exiting the plasma during the afterglow have a lower divergence angle, due to the vertical acceleration and low T@sub e@. The ion drift tube downstream of the plasma was found to be a "natural filter" to effectively screen out ions in the wings of the energy and angular distributions, allowing a directional and nearly mono-energetic ion beam to reach the sample. This work was supported by the National Science Foundation (NSF-NIRT-0303790).

4:20pm **PS-ThA8 Ion Energy Selection in Expanding Thermal Plasmas by Means of Pulse-Shaped Substrate Bias*, M.A. Blauw*,** *A.H.M. Smets, M. Creatore, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Pulse-shaped substrate bias was applied to the expanding thermal plasma. In contrast to a sinusoidal RF-waveform, a pulse-shaped RF-waveform can result in a mono-energetic ion flux to the substrate at much lower frequencies.@footnote 1@ A nearly constant substrate potential was observed between two consecutive pulses for argon-hydrogen and argon-oxygen gas mixtures. It implies that the ion flux is nearly mono-energetic because the plasma sheath transit time is much shorter than the pulse period. The ions that reach the substrate during the pulse have energy comparable to the ions at floating potential so that they do not influence the surface processes significantly. All details of the observed substrate potential can be fully described with the equivalent circuit diagram of the substrate bias system. Besides, the ion current density was derived from the linear voltage increase over the coupling capacitor between two consecutive pulses. The absolute ion density was calculated from the measured ion current density using the electron temperature of the bulk plasma. In contrast to a 13.56 MHz sinusoidal substrate bias, which creates a bright glow around the substrate, the pulse-shaped substrate bias does not influence the plasma visibly. The pulse-shaped substrate bias is particularly suitable to improve the properties of several plasma-deposited materials. The reason is that a mild ion bombardment enhances the rearrangement of surface atoms into an ordered structure, whereas highly energetic ions cause permanent damage.@footnote 2@ For example, the pulse-shaped substrate bias could be used to reduce the defect density in amorphous silicon, to increase the compactness of silicon oxide films on polymers, and, to improve the hardness of diamond-like carbon coatings. @FootnoteText@ @footnote 1@S.B. Wang and A.E. Wendt, J. Appl. Phys. 88, 643 +(2000). @footnote 2@J.W. Rabalais et al., Phys. Rev. B 53, 10781 (1996).

4:40pm **PS-ThA9 A Toroidal Plasma Source for Generation of High Throughput, Low Contamination Atomic Gases*, X. Chen*,** *W.M. Holber, P. Loomis, J. Gunn, S.Q. Shao,* MKS Instruments, Inc.

A high power, low-field toroidal RF plasma source has been developed for generation of activated gases, such as O, H, N and F. In the plasma source, RF power is coupled through ferrite cores into the plasma that acts as a secondary of an RF transformer and is confined within a toroidal quartz chamber. A combination of toroidal plasma geometry, a quartz plasma chamber, and extremely low electric field (<8 V/cm) minimizes chamber surface erosion and associated contamination. More than twice as much of atomic oxygen is generated as compared with the current generation of remote plasma sources, resulting in 2-3 times increase in throughput for photoresist stripping. Other applications include gate dielectric modification, atomic layer deposition, annealing, and wafer cleaning. This paper characterizes the plasma source and its operation with O@sub 2@, N@sub 2@, H@sub 2@, H@sub 2@O, H@sub 2@/N@sub 2@ and H@sub 2@/He gasses. Experimental measurements of plasma density and atomic gas flux of O, N, and H, using Langmuir probes, recombination probes and calorimetry, are presented. Typical plasma density is in the order of 10@super 13@ cm@super -3@. Transport of the charged species and activated neutral species through quartz and sapphire ducts, materials commonly used as liners in semiconductor process chambers, are also reported.

5:00pm **PS-ThA10 Characterization and Modeling of a Transformer-Coupled Toroidal Plasma Source for Remote Chamber Cleaning***, **B. Bai**, J.J. An, H.H. Sawin,* M. I. T.

The transformer-coupled toroidal plasma source is widely used for remote cleaning of Chemical Vapor Deposition(CVD) chamber, in which fluorine containing gases are dissociated to form fluorine atoms for downstream etching. It was found that with the addition of a small amount of N2(0.5% of the total flow) into the fluorocarbon plasmas(C2F6 or C4F8), the etching rate of silicon dioxide film was doubled, making the etching rate comparable to NF3 plasmas under the same conditions. The increase of etching rate of silicon dioxide when N is added is due to the surface modification of the transfer tube between the source and downstream chamber, where N atoms or N containing radicals block the recombination site to form COF2 and favors the formation of CO2 thereby causing more fluorine atoms to be delivered to the downstream chamber. The toroidal plasma source was experimentally characterized. Rovibrational bands of N2 and C2 were fitted to obtain the neutral gas temperatures for NF3 and C2F6 plasmas, and they were found to be in the range of 3000-6000K, which is consistent with the high power density(>15W/cm3) coupled into the plasmas. The electron temperatures were found to be 1-4 eV, as determined by the line ratios of atomic argon spectrum. The concentrations of fluorine and oxygen atoms in the plasma source were measured by the actinometry technique and other species were detected by both the Mass Spectrometer and the FTIR. It was found that NF3, C2F6, C4F8 all had nearly 100% dissociation while CF4 had only about 50% dissociation, which makes CF4 unfavorable for the remote cleaning. Global and 1-D models were set up to simulate the toroidal plasma source as an infinite cylindrically symmetrical DC positive column. Detailed plasma chemistries were considered and first three moments of the Boltzmann's equations were applied to decide the equilibrium condition of the plasmas. The model was found to explain the experimental trend very well.

Friday Morning, November 4, 2005

Plasma Science and Technology
Room 302 - Session PS-FrM
Plasma Surface Interactions III

Moderator: J. Caughman, Oak Ridge National Laboratory

8:20am **PS-FrM1 Flexible Organic Electronics: the Role of Plasma Deposition in Multi-Layer Permeation Barrier Technology***, **M. Creatore,** V.I.T.A. Lohmann, M.A. Blauw,* Eindhoven University of Technology, the Netherlands*; M.M. Koetse, H.F.M. Schoo,* TNO Science and Industry, the Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, the Netherlands

The multi-layer system of alternated inorganic and organic layers is the state-of-the-art technology for flexible organic electronics where water vapor transmission rates down to 10@super -6@g/m@super 2@day are demanded. Under debate is the role of the organic layer, which appears crucial in affecting the growth of the inorganic film, as well as the multi-layer mechanical performance. In this framework, plasma technology has not been yet fully explored; however, it is expected to contribute to the improvement of a multi-layer system design because of the development (and, ultimately, the control) of a polymer/ inorganic layer interphase region. In this contribution we report on the studies performed by means of in situ real time diagnostics (e.g., spectroscopic ellipsometry) during the plasma deposition of inorganic (SiO@sub 2@) moisture barrier layers on polymers (poly(ethylene 2,6 naphtalate)), as well as during the growth of the organic (silicone-like) interlayer. The layers are deposited in an Ar-fed expanding thermal plasma, where the deposition precursors (hexamethyldisiloxane and oxygen) are injected downstream and negligible ion bombardment (< 2 eV) takes place at the substrate. In these conditions, a polymer/SiO@sub 2@ interphase region develops, attributed to a sub-surface polymer modification during the initial film growth by means of a non- depositing radical (O, OH) flux competitive with the depositing radical (Si, SiO) flux towards the substrate. The effect of ion bombardment (either delivered with an average ion energy or a narrow ion energy distribution), as provided by externally biasing the substrate, is also under investigation. Its effects on the interphase region as well as on the roughness evolution, both strictly related to the multi-stack moisture permeation and mechanical performances, will be addressed.

8:40am **PS-FrM2 Effect of Chamber Wall Condition for Organic Film Etching Using N@sub2@/H@sub2@ Plasma***, **K. Oshima**, T. Tatsumi, K. Nagahata, K. Shinohara,* Sony Corp., Japan

We investigated the relationship between N/H plasma and the wall conditions in a dual-frequency capacitively coupled plasma system. Organic low-k film is normally etched using N-H based plasma (N@sub2@/H@sub2@, NH@sub3@), which is difficult to control because the H radical density greatly depends on the chamber wall conditions. Obtaining an accurate critical dimension and suppressing damage induced by the plasma requires precise control of the low-k materials. We found that when Cu was redeposited on the chamber walls during stopper layer etching, the etch rate of the organic film was drastically decreased, presumably because the H radicals were immediately lost at the conductive surface. To clarify the reaction mechanism between H radicals and Cu, we analyzed the optical emission of H, N, and O in H@sub2@/Ar, N@sub2@/Ar, and O@sub2@/Ar plasma, respectively, with varying area ratios (Ra) of Cu on the Si wafer (from 1 to 100%). The emission of H clearly decreased with increasing Ra, while the N and O radical densities did not change. We also analyzed the reaction mechanism between C-F polymer and Si. When there was C-F polymer in the chamber, both O and H radicals showed relatively low density because the polymer consumed both spontaneously. Since N radicals need ion energy to react with C-F polymer, they have less dependency on the chamber wall conditions. After the polymer was cleaned with O@sub2@ plasma, the optical emission spectra intensity of H gradually decreased because the slight oxidation of the top electrode surface was reduced by H@sub2@ plasma exposure, and the conductive surface started to react with the H radicals. The wall conditions thus greatly affect the H radical density. Consequently, to realize stable processes, it is important to control both the generation of H radicals due to collisions between electrons and atoms or molecules and the loss of H radicals that react with the C-F polymer or metal on the chamber wall.

9:00am **PS-FrM3 Comparison of Hydrocarbon and Fluorocarbon Polyatomic Ion Beam Treatment of Polystyrene***, W.-D. Hsu, I. Jang, **S.B. Sinnott**,* University of Florida

Plasma processing is widely used to chemically modify polymer surfaces and deposit thin films. It is well-accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma. Here, the detailed chemical modifications that result from of the deposition of beams of polyatomic fluorocarbon ions (C@sub 3@F@sub5@@super +@ and CF@sub 3@@super +@) and hydrocarbon ions (C@sub 3@H@sub 5@@super +@ and CH@sub 3@@super +@) on polystyrene surfaces at experimental fluences are identified using classical molecular dynamics (MD) simulations. The simulations make use of a reactive bond-order potential for hydrocarbons that has been extended to include fluorine and an optimized MD program. Based on the predicted accumulation of ion-surface collisions and accompanying chemistry, we elucidate how the unique chemical properties of the incident ions affect surface modification. We also determine the important differences and similarities in the chemical interactions of fluorocarbon and hydrocarbon ions with the polystyrene. This work is supported by the National Science Foundation through grant number CHE-0200838.

9:20am **PS-FrM4 Comparison of Surface Reactivity of CN, NH, and NH@sub 2@ Radicals during Deposition of Amorphous Carbon Nitride Films from r.f. Inductively Coupled Plasmas***, **D. Liu**, I.T. Martin, J. Zhou, E.R. Fisher,* Colorado State University

Carbon nitride films have received much attention because it has been proposed that the bulk modulus of @beta@-C @sub 3@N @sub 4@ may be greater than that of diamond. A number of groups have subsequently attempted to deposit carbon nitride films using various plasma techniques. However, the film deposition processes and their relationships with film properties are less studied. Here, the interactions of CN, NH, and NH @sub 2@ radicals with the carbon nitride film surface during r.f. inductively coupled plasma deposition were compared using the imaging of radicals interacting surface (IRIS) technique. Surface scattering coefficients, S, were obtained for various gas compositions of N @sub 2@+CH @sub 4@, and NH @sub 3@+CH @sub 4@, and r.f. powers. The S values of CN and NH radicals range from 0-0.15 and 0.8-0.9, respectively, and show very little dependence on the gas compositions and applied power. In contrast, the S values of NH @sub 2@ decrease from 0.8 ±0.1 to 0.4 ±0.1 when the CH @sub 4@ fraction in the plasma is increased. The essentially 100% scatter measured for NH suggests that NH is not a major deposition precursor in these plasmas. The effects of ion energies on S values were analyzed using DC bias of the substrate. The S values show an obvious dependence on the bias voltage. The r.f. inductively coupled plasmas during the film deposition have also been characterized during the film deposition by optical emission spectroscopy and mass spectrometry. Ion energy distributions were also measured using mass spectrometry. Results indicate that energetic ions are important in surface production of the species studied with IRIS. X-ray photoelectron spectroscopy analysis of deposited films showed the N content increases with increasing the N @sub 2@ or NH @sub 3@ fractions of reactive gases. The mechanisms for film deposition in these carbon nitride systems will be discussed in light of our gas-phase, surface, and gas-surface interface data.

9:40am **PS-FrM5 Real-time, Nonintrusive Monitoring of Drifting Ion Energy and Flux in a High-Density, Inductively Coupled Plasma Reactor***, **M.A. Sobolewski**,* National Institute of Standards and Technology

Measurements of the radio-frequency (rf) current and voltage applied to a plasma reactor, interpreted by plasma sheath models, provide an ability to monitor the total ion flux and ion energy distribution at surfaces inside the reactor. Such measurements are useful for monitoring drift in manufacturing or laboratory reactors when direct measurements of ion flux or energy are impossible or impractical. In this study rf measurements were used to monitor drift in Ar and Ar/CF@sub 4@ discharges in an inductively coupled, high-density plasma reactor. One source of drift in such reactors is the deposition of a conductive surface layer on the dielectric window of the inductive source. As this layer grows, a greater fraction of the source power excites currents in the layer, rather than in the plasma, resulting in less efficient operation and a reduction in plasma density and ion flux. These changes in turn affect the coupling of rf bias power into the discharge, producing changes in delivered rf bias power or voltage, sheath voltages, and ion energy distributions. Using rf measurements, the resulting changes in ion flux and energy were monitored in real time, as a surface layer was deposited. Changes in ion energies as large as 100 eV were observed. Increases as well as decreases in ion energies were observed, depending on rf bias conditions. Three different mechanisms that explain the changes in ion energies were identified. The application of the technique to monitoring process drift or irreproducibility caused by factors other than deposition on the dielectric window will also be discussed.

10:00am **PS-FrM6 Saturation of Etching Rate in Downstream Plasma Chamber Cleaning**, ***J.J. An**, B. Bai, H.H. Sawin,* MIT

NF3 and fluorocarbon downstream plasmas were investigated to study downstream chamber cleaning system. As the flow rate of NF3 increases, the etching rate of TEOS increases; however, the etching rate saturated at a given sample temperature. Flamm (1979) showed the etch rate of fluorine is a linear function of the density of F atoms, but did not observe the saturation regime. Under chamber cleaning conditions, the etching rate can be saturated, particularly on the walls where the temperature is lower than in the electrode region. Therefore an understanding of this phenomenon is critical to understanding the rate limiting processes for chamber cleaning. The etching rate was modeled using a physisorbed precursor state in which atomic F is weakly bound to the surface. The physisorbed F reacted with the fluorinated surface in a sequential reaction with a particular reaction step being rate limiting. The reaction model gives the expected first order response with atomic F concentration that was observed by Flamm at low atomic fluorine concentrations in which the etching rate is limited by the combination of adsorption equilibrium and reaction rate. At sufficiently atomic F concentrations, the surface becomes saturated and the etching rate is limited by the surface reaction rate alone. Using these surface kinetics, a well mixed reactor model was used to compute the cleaning of chambers in which surface areas of differing temperatures are exposed to the same atomic F concentration. The results for this model will be discussed for both NF3 and fluorocarbon cleaning of PECVD reactors.

10:20am **PS-FrM7 Depletion of Plasma-Induced Charge on Semiconductor Dielectrics using Ultraviolet and Vacuum Ultraviolet Radiation**, ***G.S. Upadhyaya**, J.L. Shohet, J.L. Lauer, R.W.C. Hansen,* University of Wisconsin-Madison

Radiation-induced charging during the processing of semiconductor materials can adversely affect device reliability. We have reported previously that vacuum ultraviolet (VUV) radiation with energies between 7-30eV can cause ionizing collisions in the dielectric creating charge carriers, thereby increasing the dielectric conductivity. However, the most dominant form of plasma-induced damage on a semiconductor dielectric is from electron and ion bombardment. As technology progresses, is more problematic because of increasing feature aspect ratios, Ions tend to collect at the bottom of high-aspect-ratio trenches while the lighter electrons crowd the trench walls, thus "shading" the ions. This electron-shading effect is not well documented due to the lack of a reliable diagnostic. In-situ techniques for depleting plasma-deposited charge will be an invaluable tool for manufacturing high quality devices. To this end, a technique for depleting plasma-induced charge by exposing plasma-charged wafers to either ultraviolet (UV) or VUV has been developed. Photons with energies ranging from 5-12eV possess sufficiently large penetration depths so as to photo-inject carriers from the substrate and thus deplete the previously deposited charge by conductive effects. Silicon wafers with silicon oxide or silicon nitride of thicknesses between 200 and 3000 Å grown on silicon were precharged to range of surface potentials of the order 4-10 volts by exposure to a 13.56 MHz RF plasma. The wafers were then exposed to synchrotron radiation with photon energies between 5-12 eV. From the comparison of the surface potential distributions before and after UV/VUV exposure, it is possible to determine the penetration depth of the VUV, the conditions for photoemission and photoconductivity, as well as the effectiveness of charge depletion as a function of photon energy and dielectric thickness. @FootnoteText@ Work supported by NSF under grants DMR-0306582. and DMR-0084402.

10:40am **PS-FrM8 Investigating the Interaction of High-Pressure, High Temperature Plasmas with Propellant Surfaces through Experimental Modeling**, *R. Valliere, A. Dyachenko, **R. Blumenthal**,* Auburn University

The electrothermal chemical (ETC) ignition of propellants has many advantages over conventional ignition, the most remarkable is a short, highly-reproducible ignition delay. ETC ignition results from the impingement of a multi-millisecond long pulse of high-pressure, high-density atomic plasma on the surface of the propellant. The plasma is generated by the nearly complete ablation of a polymer tube as a large capacitor is discharged through it. Direct determination of the chemical and physical processes responsible for the beneficial properties of ETC ignition would require surface sensitive probes capable of penetrating a plasma pulse that has pressures up to 33 MPa and temperatures as high as 30,000 K.@footnote 1@ In the absence of suitable probes, one must find an alternative approach. An often overlooked alternative to direct measurement is experimental modeling, pioneered by Winters and Coburn.@footnote 2@ Experimental modeling consists of replacing a complex and/or impenetrable environment with one or more of its individual components, generated in a way that is compatible with traditional surface probes. In the study of plasma ignition, the challenge is to find a vacuum compatible replacement for the ETC source output. In this work, atomic plasmas with composition and pressures close to those of the plasma pulse are created by laser ablation of thin polymer films deposited directly on the surface of the propellant. The chemical products of the nanosecond-long plasma with the propellant surface are monitored by mass spectrometry and the resulting surface is examined by XPS and Auger with the results compared to those found after truncated ETC ignition. @FootnoteText@ @footnote 1@ M. Nusca, M.J. McQuaid and W.R. Anderson, J. Thermophys. Heat Trans. @bold 16(1)@,157 (2002).@footnote 2@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

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