Plasma Science and Technology
Room 213A - Session PS1-MoM

Low-k Dielectric Etching
Moderator: B. Turkot, Intel

8:20am **PS1-MoM1 Etching of SiC and SiCN with Tetrafluoroethane/Oxygen Reactive Plasma***, **H.C. Galloway**,* Texas State University, us*; K.P. Radican,* Trinity College Dublin, Ireland*; J.M. McDonald, C. Martinez, D. Donnelly, D.C. Koeck,* Texas State University

Two materials, SiC and SiCN, are being increasingly considered as barriers for low dielectric constant materials in integrated circuit systems. It is important for researchers to be able to effectively remove these barrier layers to provide ohmic contact to the silicon substrate. The etch rate as a function of oxygen concentration was investigated in the RF magnetron plasma etching of SiC and SiCN with tetrafluoroethane gas. The etch rate and surface roughness were measured with atomic force microscopy, while evidence of polymer deposition or other surface contamination was analyzed with FTIR. Etch rates of > 10 nm/sec can be achieved with high selectivity with respect to an aluminum mask, and near infinite selectivity with respect to silicon. This process has been demonstrated to be compatible with producing test structures of aluminum contacts to measure the electrical properties of some low-k materials. Tetrafluoroethane is of interest due to its high fluorine content. It is also a nontoxic, ozone friendly gas with a short atmospheric lifetime. The role of oxygen in the etching process will be discussed and this etching process will be compared to other similar etches that have been previously reported.

8:40am **PS1-MoM2 Investigation of Fundamental Etching Reaction of Organic Low Dielectric Film Using Ion Beams with Radical Injection***, **M. Yuuhei**, H. Masaru, G. Toshio,* Nagoya University, Japan*; A. Atsuhiro, T. Tetsuya,* Sony Co, Japan

Etching of organic low dielectric (low-k) interlayer films has been an essential process in ULSIs. However, this process becomes more complex and requires the high accuracy. Therefore, quantitatively understanding of this process is very important. Low-k etching using plasma, it is impossible to control the radicals and ions independently and so it is difficult to clarify the etching mechanism quantitatively. In this study, the ion beam apparatus with radical injection was developed and applied to the investigation of fundamental reaction of organic low-k film. The apparatus is composed of Ar@super +@ beam source, electron shower gun, and radical injection source. A compact electron cyclotron resonance plasma source was used as a radical source. To remove the electrons and ions in the plasma, two retard electrodes were installed in front of the plasma source. Using the vacuum ultraviolet absorption spectroscopy, the absolute densities of H and N radical generated by radical source were evaluated. Etching sample was blanket film of SiLKTM. The etching subsurface reactions were measured by in-situ XPS. The etch rate by Ar@super +@ beam was enhanced by the injection of H and N radicals. Especially, the etching rates of injection of mixing radicals of H and N were high comparing with those of H or N radical. The C=N/C-N ratio of subsurface was increased with increasing N radical and H+N radical density under the Ar+ ion bombardment When H+N radical was injected under the high ion energies above 300eV, the C=N/C-N ratio was higher than those under the low ion energies. Consequently, the high C=N/C-N ratio of the subsurface is a key factor for the high etch rate of the organic low-k film.

9:00am **PS1-MoM3 Fluorocarbon Surface Chemistry in Dual Frequency Capacitively Coupled Discharges for Dielectric Etching: A Comparison with Inductively Coupled Plasmas***, **L. Ling**, X. Hua, L. Zheng,* University of Maryland at College Park*; G. Oehrlein,* University of Maryland at College Park, US*; E.A. Hudson,* Lam Research Corp.*; P. Jiang,* Texas Instruments Inc.*; P. Lazzeri, M. Anderle,* ITC-irst, Italy*; Y. Wang,* National Institute of Standards and Technology

Mechanically confined dual-frequency capacitively coupled plasma (DFCCP) reactors featuring a high frequency powered electrode for plasma production and low frequency RF biasing for ion bombardment control of the substrate are increasingly being used for fluorocarbon (FC) plasma-based pattern transfer into SiO@sub 2@ and low k dielectric materials. We describe a study of confined DFCCP properties fed with C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 6@/Ar. In particular, we compare the chemistry of FC films formed on various surfaces with data obtained for inductively coupled discharges. Precursor gas dissociation is determined using mass spectrometry. The composition of the incident ion flux is determined by ion-sampling. The deposition rates, composition and bonding of passively deposited fluorocarbon films (no etching of the substrate), and the composition, bonding and thickness of the surface reaction layers that form on SiO@sub 2@, resist and silicon surface during steady state etching are determined as a function of processing conditions using ellipsometry and X-ray photoemission spectroscopy. The influence of ion bombardment on the composition of deposited fluorocarbon films is studied by comparing FC films deposited underneath a small gap structure with those deposited on ion bombarded surfaces. The influence of pressure, RF bias and gas mixture of FC-based DFCCP on the characteristics of resist pattern transfer into organosilicate glass and nanoporous silica is also reported.

9:20am **PS1-MoM4 Low-k and Porous Low-k Sidewall Roughening: Fluorocarbon Plasma and Beam Measurements***, **Y. Yin**, S.A. Rasgon, H.H. Sawin,* Massachusetts Institute of Technology

For the patterning of sub 100 nm features, a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable, both from a fundamental as well as a manufacturing perspective. Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. It is this post-etch sidewall roughness which will ultimately affect device performance. The integration of organosilicate glass (OSG) and porous OSG films as low-k interlayer dielectrics presents new challenges from a roughening standpoint, particularly when using highly polymerizing fluorocarbon plasma chemistries typical of oxide etching. Under certain conditions the added carbon present in OSG films can increase localized deposition, yielding both carbon-rich and substrate-rich areas of the sample, and creating surface roughness based on the etch selectivity difference (polymer micromasking). Additionally, fluorocarbon polymer can be seeded into the pore structure of porous OSG films, magnifying the effect. We have previously examined this effect on planar samples in a conventional plasma etcher. However, the role of fluorocarbon polymerization on sidewall roughening/striation of OSG/porous OSG has not been investigated. Therefore, we have undertaken an examination of this sidewall roughening using a new, inductively coupled plasma beam source. This source allows the exposure of a sample to a realistic ion and neutral flux, of any desired plasma chemistry, while allowing independent control of the ion bombardment energy and incident angle. By rotating the sample to a near-glancing angle, a sidewall can be simulated, eliminating any effects associated with patterning. The effects of ion bombardment, impingement angle, and fluorocarbon chemistry (highly polymerizing vs. low polymerizing) on the roughening of SiO2, OSG, and porous OSG are discussed. Finally, insight into the surface roughening mechanism is obtained through modeling.

9:40am **PS1-MoM5 The Effects of Pore Morphology on the Diffusive Properties of a Porous Low-K Dielectric***, **E.A. Joseph**, M.J. Goeckner, L.J. Overzet,* University of Texas at Dallas*; D.W. Gidley,* University of Michigan*; B.E.E. Kastenmeier,* IBM/International Sematech

Porous methylsilsesquioxane-based spin-on films with pore sizes of 1.5 - 2 nm and porosities ranging from 0 - 31% have been exposed to fluorocarbon and oxygen plasma chemistries to determine the integratability of the films. Using both spectroscopic ellipsometry and Auger electron spectroscopy, the porosity of the modified films was found to decrease during fluorocarbon and oxygen plasma exposure due to fluorine in-diffusion and carbon depletion, respectively. The depth of these compositional modifications is also measured and correlated to the porosity and pore interconnectivity, determined from Positronium Annihilation Lifetime Spectroscopy. Parallel studies of TaN atomic layer deposition also reveal tantalum in-diffusion, with diffusion lengths ranging from 40 - 125 nm (depending on porosity), and are comparable to those of fluorine, indicating that the diffusion and depletion lengths are governed by pore size and interconnectivity and are not material dependent. Lastly, moisture uptake in these films was examined and found to significantly affect both the overall porosity of the unprocessed films as well as the diffusion and depletion lengths of fluorine and carbon. @FootnoteText@ This work is supported by a grant from NSF/DOE, CTS-0078669.

10:00am **PS1-MoM6 Using In-vacuo Electron-Spin-Resonance and Infrared Spectroscopy Technique in the Analysis of Surface Reactions of Low-k films during/after Plasma Processes***, **K. Ishikawa**,* Tohoku University, Japan*; Y. Yamazaki, S. Yamasaki,* AIST, Japan*; T. Ozaki, Y. Ishikawa, S. Noda, S. Samukawa,* Tohoku University, Japan

Using in-vacuo electron-spin-resonance (ESR) and infrared spectroscopy (FT-IR) techniques, surface reactions of low-k (porous methylsilsesquioxane, MSQ) films during/after plasma processes were

studied. To understand the reaction mechanism on the surface with impinging species as ions, radicals, and photons, creation of dangling bonds (DBs), namely, bond breaking, is indeed a key process. The created DBs are playing an important role for surface chemical reactions. Applying our knowledge about pure SiO@sub 2@, the extensive study was made with respect to the porous MSQ, which is a candidate for future 45 nm node devices. Samples were prepared by spin-on coating a film of porous MSQ, on a bare Si substrate. The substrate was placed in a parallel-plate type reactor. Plasma discharge was sustained for proccessing. Since the DBs are affected by air exposure, our in-vacuo measurement needs to observe real feature of DBs. Thus, soon after the plasma process, an ESR spectrum was measured following transferring to the ESR cavity under vacuum ambient. Carbon-DB in the film is identifiable from g-value of the ESR signal. This indicates that the plasma process creates easily carbon-DBs, which has a highly chemical reactivity with oxygen.@footnote 1@ We also carried out an experiment using FT-IR. On an infrared spectrum of the film after the process, the decrease of the peak arising from Si-CH@sub 3@ bonds was clearly observed. Tentatively, we speculate that not only reactive species but also plasma characteristics as emissions affects to creation of the carbon-DBs and the created C-DBs plays an important role for the surface modification during/after the plasma process. @FootnoteText@ @footnote 1@ K. Ishikawa, et al. Appl. Phys. Lett. 81, 1773 (2002).

10:20am **PS1-MoM7 Minimizing low-k Damage during In-situ Photoresist Strip***, **E.A. Hudson**, T. Choi, O. Turmel, L. Zheng, K. Takeshita, S. Lee, P. Cirigliano,* Lam Research Corp.

To increase the speed of devices, microelectronics fabrication is shifting to low-k dielectric materials as insulators for interconnect layers. k values may be reduced below ~3.0 using carbon-doped materials such as organosilicate glass (OSG). k is further reduced, below ~2.5, by introducing pores in the film. Problems may arise, however, because carbon is easily removed from these materials during plasma processing, specifically during the etching of lines and vias, and the photoresist strip after etch. Carbon loss causes an increase in the dielectric constant and thus degrades device performance. This paper focuses on the damage trends for carbon-doped dielectrics arising from in-situ photoresist strip in a capacitively-coupled dielectric etch system. Microscopic test structures have been developed, which allow direct measurement of the intrinsic damage which results from the interaction of the plasma strip environment with the unprotected and unmodified sidewall of a trench. Damage trends have been evaluated as a function of pressure and frequency of RF excitation during the strip. Damage is minimized for pressures in the 10 - 50 mTorr range. Etch processes typically leave a polymer coating on the sidewall of trenches and vias. This sidewall passivation is found to greatly reduce the low-k damage induced by the strip process. Ultimately the polymer must be removed from the sidewall to allow subsequent fabrication steps, but during the strip this film acts as a protective barrier against low-k damage. Therefore an overall strategy for minimizing damage is to run a low pressure strip, under conditions which preserve sidewall passivation as long as possible.

10:40am **PS1-MoM8 Comparison of In-situ and Ex-situ Resist Strip Process for Ultra Low-k/ Cu Interconnect***, **H. Xu**, A. Shen, V. Tarasov,* ULVAC Technologies*; B. White, J. Wolf,* International Sematech

According to the ITRS roadmap, ILD layer with effective dielectric constant (k@sub eff@) of < 2.7 will be needed for 65 um technology node for high performance logic devices. To achieve k@sub eff@ of < 2.7, ultra low-k film with bulk k of < 2.1 will be needed. One of the challenges in integrating the ultra low-k material is the susceptibility of low-k material to damage from the post etch resist ashing and residue clean process. Directional resist ashing at low wafer temperature may provide a solution for avoiding damage to ultra low-k materials. Directional resist ashing can be done either in situ in a low-k etch chamber or ex situ in a standalone ash chamber. In this paper we will compare the process results between in situ and ex situ resist ash for ultra low-k film. The N@sub 2@/H@sub 2@ in situ ashing was done in a low k etch chamber which is a magnetically enhanced RIE reactor. The O@sub 2@ based ex situ ashing was done in a plasma chamber on an asher platform. This chamber incorporates a WCP plasma source and an independent wafer RF bias for independent plasma density and ion energy control. The WCP source was an ULVAC designed inductively coupled plasma source for achieving higher plasma density and lower electron temperature than a conventional ICP source. One experiment with an N@sub 2@/H@sub 2@ chemistry shows that while both in situ and ex situ resist ash shows comparable RC products. The RC product is an indirect measure of k@sub eff@, obtained from serpentine and comb test structure of 0.125/0.175um line width/spacing, indicating equally low damage to the ultra low-k film by the ash process. The ex situ N@sub 2@/H@sub 2@ ash process caused much less corner rounding of the SiC cap layer . Another experiment using a dilute O@sub 2@ ash process, shows that the RC product is sensitive to the chamber conditions used for resist ashing, suggesting mixing low k etch with O@sub 2@ based resist ash in the same chamber may cause more damage to ultra low-k film.

11:00am **PS1-MoM9 Impact of Different Ashing Plasmas on Porous and Dense SiOCH***, **T. Chevolleau**,* LTM-CNRS, France*; N. Posseme,* STMicroelectronics, France*; T. David, O. Joubert,* CNRS/LTM, France*; O. Louveau,* STMicroelectronics, France*; D. Louis,* CEA-LETI, France

In CMOS technology, the introduction of porosity into Low-k dielectric is the dominant strategy to achieve future generation of ultra low K interlayer dielectric materials (k~2.2). One of the integration challenges with these new materials are their structural modification during the etch and stripping processes due to a higher sensitivity with respect to the plasma . This study is dedicated to the impact of ash processes on a non porous SiOCH (k = 2.9) and a porous SiOCH (k=2.2, 50% void). The ash processes were carried out on blanket wafers either in a Magnetically Enhanced Reactive Ion Etcher using O@sub2@ and NH@sub3@ plasmas or in a photoresist stripper using H@sub2@ and O@sub2@ based downstream microwave plasmas. After plasma exposure, the surface and bulk modification of SiOCH films are investigated using quasi in-situ X-Ray Photoelectron Spectroscopy, Attenuated Total Reflection spectroscopy, Spectroscopic Ellipsometry and contact angle. The results show that the degree of SiOCH bulk modification is related to the carbon depletion and the moisture adsorption in the remaining film after plasma exposure. The materials are not altered in an H@sub2@ based plasmas without nitrogen whereas a film degradation is clearly pointed out in O@sub2@ based plasmas. When N@sub2@ is added to O@sub2@ or H@sub2@ plasmas, the porous film degradation is significantly enhanced. These results reveal that the best ash chemistries are H@sub2@/Ar and H@sub2@/He gas mixture. The P.R stripping feasibility on porous SiOCH films integrated in a single damascene structure is also performed and electrical results demonstrate that NH@sub3@ and H@sub2@/He ashing chemistries minimize the degradation of porous SiOCH compared to oxygen containing gas mixtures. Furthermore, Energy Filtred Transmission Electron Microscopy analyses reveal an efficient pore sealing with the NH@sub3@ chemistry leading to the elimination of TiN diffusion through the pores during barrier deposition.

11:20am **PS1-MoM10 Analysis of Ash-Induced Modification of Porous Organosilicate Glass Inter-Level Dielectric Materials on Patterned Structures Utilizing Electron Energy Loss Spectroscopy and Angular Resolved XPS***, **N.C.M. Fuller**, T.J. Dalton,* IBM TJ Watson Research Center*; C. Labelle,* Advanced Micro Devices Inc.*; M.A. Worsley,* IBM TJ Watson Research Center, Stanford University*; D. Dunn, T.S.L. Tai,* IBM Microelectronics Division

We have previously illustrated the need for analyzing patterned structures versus blanket wafers to effectively understand the dominant mechanism(s) effecting inter-level dielectric (ILD) modification during photoresist removal for damascene processing. The evolution of CMOS technology to maintain the ITRS roadmap potentially demands the introduction of porous (OSG or SiCOH)-based materials which are even more susceptible to ash-induced modification than their dense counterparts; as a consequence, the demand not only for finding a suitable ash solution (for specific integration schemes), but also for completely understanding the dominant mechanism(s) that modify these porous films is quite critical. Work to date by these authors has concentrated on analyzing ash-exposed ILD surfaces via electron energy loss spectroscopy (EELS) and examining the chemical changes in the surface as a function of ash chemistry/conditions. This work will summarize recent efforts aimed at further unraveling the mechanism(s) that influence the modification of relevant porous OSG-based ILD materials via the use of both EELS and the more sensitive angular resolved XPS (AR XPS) on both 200mm and 300mm patterned wafers. Relevant results will be presented.

11:40am **PS1-MoM11 Highly Selective Etching of Si@sub 3@N@sub 4@ to SiOC by Precise Ion Energy Control for sub-90 nm Dual Damascene Formation***, **H. Hayashi**, A. Kojima, A. Takase, K. Yamamoto, I. Sakai, T. Ohiwa,* Toshiba Corporation, Japan

Sub-90nm LSIs designed for high speed and low power operations, demand introduction of low-k material for interlayer dielectric material. We have reported that the 100 MHz rf capacitive coupled plasma (CCP) RIE process is the most suitable for etching organic film because of its low ion energy@footnote 1@@super ,@@footnote 2@. Furthermore, for low-k SiOC film etching which requires a higher energy etch process, we have

developed dual frequency superimposed (DFS) 100 MHz and 3.2 MHz rf CCP etch processes, which can control electron density and self-bias voltage independently in a wide range. In the damascene etch process of SiOC film using Si@sub 3@N@sub 4@ as etch mask, it was observed that the mask edge erosion is strongly dependent on ion energy regardless of selectivity. An excellent etch profile, as well as selectivity was realized by precise ion energy control@footnote 3@. We have newly developed a highly selective Si@sub 3@N@sub 4@ to SiOC etch process with CF@sub 4@/H@sub 2@ gas chemistry, which requires the reverse selectivity. Such a selective etch process enables dual damascene interconnects formation with a much lower dielectric constant. The blanket SiOC etch rate decreased as H@sub 2@ addition to CF@sub 4@ was increased, and became zero when the H@sub 2@ flow rate was equal to the CF@sub 4@ flow rate. The blanket Si@sub 3@N@sub 4@ etch rate did not decrease with H@sub 2@ addition, so high selectivity was achieved, regardless of ion energy. Next, this highly selective process condition was applied to Si@sub 3@N@sub 4@ etching using SiOC mask, where again, mask edge erosion was dependent on ion energy regardless of selectivity. Highly selective damascene etching of Si@sub 3@N@sub 4@ was realized by precise ion energy control using DFS RIE. @FootnoteText@ @footnote 1@H. Hayashi et. al., Symp. Dry. Process. (2002) p.195@footnote 2@H. Hayashi et. al., AVS 50th Symp. (2003) PS-TuA5@footnote 3@A. Kojima et. al., Symp. Dry. Process. (2003) p.13.

Plasma Science and Technology
Room 213B - Session PS2-MoM

Silicon Etching

Moderator: F. Celii, Texas Instruments

8:20am **PS2-MoM1 Challenges Facing Deep Trench Silicon Etching for Present and Future Trench Technology Nodes***, **A.M. Paterson**, S. Pamarthy, A. Khan, F. Ameri, J.Y. Chen, H. Mohiuddin, T. Panagopoulos, J.P. Holland, T. Lill,* Applied Materials, Inc.*; A. Steinbach, S. Wege,* Infineon Technologies

The reduction in trench technology nodes to 90nm and beyond brings new challenges to deep trench silicon etching of capacitor structures for DRAM applications. At present gate feature sizes of 110nm requires silicon trench etching depths of 8um, with a top critical dimension of 160nm, corresponding to an aspect ratio of 50:1. The depth, and hence aspect ratio of the trench, is determined by customer capacitor cell and leakage current requirements. In the next five years, the trench nodes will reduce further to 90nm, 70nm and 65nm with the aspect ratios of the silicon trench increasing to 65:1, 80:1 and 100:1, respectively. The shrinking of the node to smaller sizes brings new challenges to semiconductor OEMS. The technology that was used for etching trenches at one node size may not give the required trench at the smaller node size. This was found to be the case when moving from 0.35µm to 0.25µm node size where the tool of choice, AMAT DPS@super TM@ DT, had limitations in obtaining the required customer specifications for the new node. After subsequent research and development at Applied Materials, a new High Aspect Ratio Trench (HART@super TM@) chamber has shown the capability of etching trenches down to the 70nm node. This paper will discuss why the choice of plasma source, source rf frequency, bias rf frequency and chamber geometry are of critical importance in achieving such high aspect ratio trenches.

8:40am **PS2-MoM2 Etching High Aspect Ratio Structures in Si using SF@sub 6@/O@sub 2@ Plasma: Experiments and Feature Scale Modeling***, **R.J. Belen**[1], S. Gomez,* University of California Santa Barbara*; M. Kiehlbauch, D. Cooperberg,* Lam Research Corporation*; E.S. Aydil,* University of California Santa Barbara

Plasma etching of high aspect ratio structures in Si is an important step in the manufacture of memory devices and MEMS components. The goal is to etch deep features anisotropically with high etch rates, high selectivity to the mask and good uniformity. We have studied the etching of deep sub-micron diameter holes in Si using SF@sub 6@/O@sub 2@ plasma. Our approach is to combine experiments and plasma diagnostics with feature scale modeling to gain a fundamental understanding of the etching kinetics necessary to develop and scale-up processes. Etching experiments are conducted in a low pressure, high density, inductively coupled plasma etching reactor. Visualization of the profiles with SEM is used together with plasma diagnostics such as optical emission and mass spectroscopies to study the effect of pressure, rf-bias voltage and SF@sub 6@-to-O@sub 2@ gas ratio on the etch rate, selectivity and feature profile shape. Simultaneous with experiments, we have developed a feature scale model of the etching process. Information from plasma diagnostics and previously published data are used to reduce the degrees of freedom in the model by estimating F, O, and ion fluxes and ion energy and angle distributions. We have designed experiments to directly measure parameters such as the chemical etch rate constant and the etch yield dependence on the ion angle. Experimentally inaccessible parameters such as sticking coefficients and etch yields are determined by matching simulated profiles with those experimentally observed under various etching conditions. The F-to-ion flux ratio and F-to-O flux ratio are found to be the important plasma parameters that determine the etch rate and anisotropy. Plasma diagnostics provide quantitative information about the location of the ion and neutral-limited regimes in the operating parameter space. The SF@sub 6@-to-O@sub 2@ gas ratio determines the balance between etching and sidewall passivation, which controls the feature profile shape.

9:00am **PS2-MoM3 Etch Rate and Profile Evolution Model for High Aspect Ratio Etch in HBr/NF3/O2 Plasma***, **A. Kersch**, W. Jacobs, W. Sabisch, G. Schulze-Icking, A. Henke, S. Wege,* Infineon Technologies AG, Germany

Silicon etching based on a HBr/O2/NF3 plasma generated in a capacitively coupled Merie plasma reactor is used to fabricate DRAM trench capacitors. To maintain a constant capacitance per memory cell an optimum aspect ratio and trench shape with respect to capacitance and cost has to be achieved. In this paper we report about two feature scale models of different complexity. A compact model calculates the etch rate for a given trench geometry by solving an integral equation for the neutral and ion transport inside the trench. Input parameter are ion and fast neutral fluxes and their energy distribution as a function of CCP power, pressure, magnetic field, and the fluxes of reactive radicals as a function of plasma and gas flow conditions. The efficiency of this approach allows the investigation of effects of trench profile on the etch rate for a variety of data. A high level model calculates in addition the trench profile evolution as a function of the above parameters supplemented by the particles angular distribution, a surface scattering distribution, and a chemical rate model for etch and side wall passivation. These calculations are done with an axisymmetric/3D profile simulator (TOPSI3D) which used level set front propagation, Monte Carlo particle transport, and chemical surface reaction rates (1). For the selection of the input parameter, a combination of experimental values (plasma density, V-I measurement, RGA) and reactor scale simulation (plasma, neutral gas flow and collisional sheath) is used. The paper focuses on the effects of power, magnetic field, pressure and gas flow on the etch rate and trench profile. The results of both models are in good agreement with each other as well as with experimental data for several technology nodes. @FootnoteText@ @footnote 1@ W.Jacobs et al, IEDM Tech. Digest, Session 35/5, 2002 .

9:20am **PS2-MoM4 Optimal Chamber Aspect Ratio of an Inductively Coupled Plasma Etcher for Advanced Gate Application***, **Y.D. Du**,* Applied Materials Inc.

It has been known that the chamber aspect ratio (length/radius) played a significant role in defining ion flux and neutral flux uniformity (including passivaiton distribution) across the wafer in an inductively coupled plasma source. This paper will present a detailed study of silicon etch rate and CD uniformity as a function of chamber aspect ratio. Process parameters such as pressure, power and chemistry dependence on etch rate and CD uniformity are systematically compared under different chamber body length. A series of plasma modeling and gas flow modeling using a 2-D axisymmetrical fluid model are conducted and compared with the experimental data. The results show that an optimal chamber aspect ratio design requires careful balancing of plasma source uniformity as well as by-products distribution across the wafer in order to meet the overall stringent gate patterning etch requirements.

9:40am **PS2-MoM5 Highly Anisotropic and Damage-free Gate Electrode Patterning in Neutral Beam Etching Using F@sub 2@ Based Gas Chemistry***, **S. Noda**,* Tohoku University, Japan*; Y. Hoshino,* Showa Denko K.K., Japan*; T. Ozaki, S. Samukawa,* Tohoku University, Japan

Neutral beam etching is a promising candidate for the damage-free processing of semiconductor devices. To realize high-performance etching processes, we developed a new neutral beam etching system. In this system, highly efficient neutral beams could be obtained by accelerating negative ions generated in the pulse-time-modulated plasma. Damage-free 50 nm poly-Si gate electrode patterning has already been accomplished by our system using the Cl@sub 2@/SF@sub 6@ mixture gas

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

chemistry@footnote 1@. In this gas chemistry, accelerated Cl and F atoms contributed to the etching reaction and the etching profiles were controlled by changing the gas flow ratio. However, the etching rate and the pattern profile were drastically varied with changing the gas flow ratio. Especially, by increasing the SF@sub 6@ flow rate, both the etching rate and the side etching increased rapidly. There were trade-off between the etching rate and etching profile in the SF@sub 6@ based gas chemistry. Namely, SF@sub 6@ plasma generated a large amount of F radicals. To settle this problem, F@sub 2@ gas plasma was investigated to generate the fast F atom beam efficiently with maintaining low density of F radical. In comparison between F@sub 2@ and SF@sub 6@, great differences were observed in the etching characteristics. Even in the case of pure F@sub 2@ gas chemistry, the etching anisotropy drastically increased and the side etching of poly-Si hardly occurred. It is caused by elimination of the F radical generation and increase of negative ion (F@super -@) generation in the F@sub 2@ plasma. Using this feature, more flexible and precise control will be achieved in the neutral beam etching method. @FootnoteText@ S. Noda et al., to be published in J. Vac. Sci. and Technol. A, Jul/Aug (2004).

10:00am **PS2-MoM6 Silicon Recess Formation During High Density Plasma Polysilicon Gate Etching***, **S.A. Vitale**, B.A. Smith,* Texas Instruments

Silicon loss during gate etch from the active region of a traditional CMOS transistor is shown to take place through plasma oxidation of the silicon substrate during the over-etch step. The plasma oxidation occurs by an ion-enhanced process with an activation energy of only 0.02 eV. This phenomenon is successfully modeled using the traditional Deal-Grove thermal oxidation model, with the inclusion of a depth-dependent reaction rate constant to incorporate the ion-enhancement effect. Plasma oxidation and silicon loss are reduced by using a shorter poly over-etch time, lower source and bias power, lower substrate temperature, and lower O2 flow. A viable poly-over etch process was developed which produced vertical poly profiles while reducing the silicon loss by 32%.

10:20am **PS2-MoM7 Deep Cryo-Etching for Silicon Structures***, **T.T. Tillocher**, R.D. Dussart, X.M. Mellhaoui, P.L. Lefaucheux,* GREMI - Orléans University, France*; M.B. Boufnichel,* ST Microelectronics - Tours, France*; P.R. Ranson,* GREMI - Orléans University, France

Semiconductor technology requires more and more accuracy in deep etching. The cryogenic process, which uses a SF@sub 6@/O@sub 2@-based chemistry and a cryogenically cooled wafer chuck, is promised to a great future since it provides smooth profiles and high etch rates. Indeed, this cryo-etching enables to realise with these good performances different patterns on silicon and SOI wafers (vias, trenches...) for a wide range of mask openings. This process is very accurate and fastidious to control since its efficiency results from a weak equilibrium between the simultaneous etching and passivation mechanisms. If the latter is broken, defects (black silicon, notching, bowing, undercut...) can appear and grow very quickly. We will detail these different defects and their conditions of appearance. A new cryogenic chuck, associating electrostatic clamping and a very good temperature uniformity , allows the etching of very uniform profiles all over the surface of the 6'' wafers. This is a critical aspect in the project since for certain projects the two sides of the wafer have to be etched separately and the profiles, depending on the temperature, must have the same shape from one side to the other. Parallel plasma diagnostics, such as actinometry, Langmuir probe, FTIR, interferometry, are the key to a better understanding of the process and hence to better control the process. We will present our last results on projects carried out in collaboration with STMicroelectronics/Tours. Some plasma measurements will be presented and correlated to the etching performances.

11:00am **PS2-MoM9 Atomic-scale Simulations of Spontaneous and Ion-assisted Etching of Silicon***, **D. Humbird**, D.B. Graves,* University of California, Berkeley

Molecular dynamics (MD) simulations model the phenomenon of thermal halogen atoms etching silicon spontaneously, and capture the atomic-scale mechanisms of Ar@super +@ ions and neutral halogen atoms working together. Using improved interatomic potential energy functions for Si-F and Si-Cl, MD predicts steady halogen uptake and spontaneous etching as F and Cl atoms impact Si. At 300 K, the simulations agree semi-quantitatively with experimental measurements of total surface coverage, halosilyl group coverage, reaction probability, and etch product distribution. Etch products that remain weakly bound to the surface are detected in significant quantities. At higher temperature, agreement between simulation and experiment is qualitative; the simulation matches trends in reaction probability and etch product redistribution. Below 450 K, etch products form and promptly desorb. At higher temperatures, internal decomposition of the halogenated silicon layer dominates. The forthcoming phenomenological model of Winters et al. is based in part on some of the observations of our simulations@footnote 1@. Significant etching enhancements are realized when simultaneous energetic Ar@super +@ ions impact the halogenated Si surface. Si etch yields are in good agreement with experiments. The atomic-scale mechanisms of ion-enhanced etching are classified as enhanced spontaneous etching, chemically enhanced physical sputtering, and chemical sputtering. The primary effects of ions are to increase the local surface coverage of etchant species and to create products by inducing chemical reactions within the halogenated surface layer. Ion-assisted effects are most pronounced at low neutral/ion ratio and decline as this ratio increases. Explicit ion enhancements are greater for Cl than for F. @FootnoteText@ @footnote 1@HF Winters, D Humbird, and DB Graves, in preparation (2004).

11:20am **PS2-MoM10 X-ray Photoelectron Spectroscopy Analyses of SiGe and Si Surfaces after Selective Etching of Si***, **S. Borel**, O. Renault, J. Bilde,* CEA-DRT-LETI, France

Recent progress in thin films epitaxial growth enables to consider new applications based on the realisation of Si/SiGe/Si heterostuctures. Indeed, lateral etching process can removed either SiGe or Si sacrificial layer and leads to a cavity between two single crystal-layers. The empty space thus created can be filled by an amorphous material in order to obtain a mono-layer on a insulator (Silicon On Nothing transistors). The selectivity of such processes is crucial for safeguarding of transistors actives parts dimensions. The Si removal etching process is as much more interesting because the selectivity to SiGe is almost infinite. The infinitely selective isotropic etching of Si to SiGe@footnote 1@, obtained by using a combined addition of N@sub 2@ and CH@sub 2@F@sub 2@ into O@sub 2@ +CF@sub 4@ plasma was studied by ex-situ X-ray photoelectron spectroscopy. Etched Si and SiGe surfaces were analysed in terms of elemental composition, bonding states and oxide/oxyfluoride thickness by careful decomposition of Ge3d, Si2p, C1s and F1s core-level spectra. Both F1s and C1s spectra show up a component due to fluorocarbon polymeric groups, the quantity of which is 3 times higher on SiGe than on Si. At the same time on SiGe surfaces, F1s and Ge3d spectra reveal a large formation of Ge(O@sub x@)F@sub y@ bonds compared to metallic Ge, whereas SiF@sub x@ are almost absent. We conclude that a layer formed by a fluorocarbon polymer and Ge oxyfloride induces a total passivation of the SiGe when subjected to the N@sub 2@ /CH@sub 2@F@sub 2@/O@sub 2@+CF@sub 4@ plasma. The precise role of the CH@sub 2@F@sub 2@ will be tentatively interpreted on the basis of other etching results with similar inverted selectivities. @FootnoteText@ @footnote 1@ S. Borel et al., Jpn. J. Appl. Phys. (accepted).

Plasma Science and Technology
Room 213A - Session PS1-MoA

Plasma Surface Interactions in Etching

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

2:00pm **PS1-MoA1 Quantitative Plasma Beam Investigation of Polysilicon Sidewall Roughening**, ***S.A. Rasgon*[1]**, *Y. Yin, H.H. Sawin,* Massachusetts Institute of Technology

For the patterning of sub 100 nm features,a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable, particularly at the gate level where variations in line width can adversely impact the electrical performance of the device. Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. It is this post-etch sidewall roughness which will ultimately affect device performance. Our past research has focused on the observation of sidewall roughness via a novel AFM technique. The resulting images allow the extraction of quantitative information on sidewall roughness and spatial frequency as a function of depth, and vividly highlight the structure of the post-etch sidewall. While these images present a remarkable display of sidewall roughness encountered in common etching processes, a fundamental study of post-etch sidewall roughness remains elusive due to the inherent experimental difficulties encountered. Sidewall roughening during etching depends on the plasma chemistry, ion bombardment energy, and ion incident angle. A true fundamental study requires independent control of all three parameters, impossible to obtain in a conventional plasma etcher. To remedy these difficulties, an inductively-coupled plasma beam source was constructed that allows the exposure of a sample to a realistic ion and neutral flux, of any desired plasma chemistry, while allowing independent control of the ion bombardment energy and incident angle. By rotating the sample to a near-glancing angle, a sidewall can be simulated. This apparatus is used to conduct a fundamental study of sidewall roughness/striation during HBr etching of polysilicon. The resulting AFM images are analyzed for roughness magnitude/spatial frequency using a novel geostatistical technique, and are compared with real sidewalls. Finally, insight into the roughening mechanism is obtained through 3D modeling of the roughening process.

2:20pm **PS1-MoA2 3-Dimensional Feature Scale Simulation of Polysilicon Sidewall Roughening**, ***H. Kawai***, *W. Jin, H.H. Sawin,* MIT

The line edge roughening has become an important factor as the features shrink. Although there are 2-dimensional simulators that can simulate the artifacts such as faceting and microtrenching, they can not simulate the surface roughness since it is inherently 3-D in nature. Therefore, a 3-dimensional simulator was developed to study the physics of surface and line edge roughening. 2 Â½ -dimensional simulator, that had been developed before, applied Monte Carlo model to model the surface kinetics. Although 3-D simulator also used Monte Carlo model, many changes were made to convert the simulator from 2 Â½ -D to 3-D. These include a new algorithm for the computation of surface normals and fluxes on sidewalls. In addition, since 3-D simulator is more computationally intensive, it is necessary to optimize the simulator by minimizing the computation time while maintaining the accurate results. Simulation domain was discretized into cubic cells with the side of 2.5 nm, and when a particle strikes a surface cell, the local surface conformation was determined. The algorithm was based the fitting of the local region of the surface cells with a polynomial. The cell size of 2.5 nm had been used since the cell size corresponds to the ion induced mixing length. Since the grooved striations formed in line edge roughening have minimum radius of curvatures of about 25 nm, the appropriate degree of polynomial and number of cells to be fitted were selected to allow the representation of surface curvatures of 25 nm or less. This fitted surface is then used to compute the surface normal, scattering angle, and flux on the 3-D surface. The surface normal was used to determine the movement of the surface with material etching or deposition by selecting the appropriate cell for cell addition or collapse.

2:40pm **PS1-MoA3 Unraveling the Complex Process Known as 'Plasma Chemistry'**, ***M.J. Goeckner***, University of Texas at Dallas **INVITED**

'Plasma chemistry' is perhaps one of the most complex processes known. In general it can be thought of as the interaction between three main scientific subsystem, plasma physics, gas-phase chemistry/physics and surface-phase chemistry/physics. To understand this complexity one simply needs to consider how a given reactive gas-phase specie might interact with a surface. Does it stick to the surface? Does it chemically react with the surface? Does it promote film growth? How does this interaction change the gas composition? How does an altered gas-phase chemistry alter the plasma? Understanding these interactions is key to producing better models of plasmas, allowing the optimization of complete process systems and hence improved product yield. This talk will briefly review how various groups are attacking this complex problem. Then using our fluorocarbon chemistries (CF@sub 4@, C@sub 4@F@sub 8@) studies as an example, we examine how gas and surface chemistries change for different wall conditions (temperature, diameter and material) as well as gas flows and plasma parameters. Based on this knowledge, we will discuss possible interaction mechanisms and how these might affect the process. This will in turn lead to a discussion of possible future studies. This work is supported by a grant from NSF/DOE, CTS-0078669.

3:20pm **PS1-MoA5 Stabilization of Radical Composition Drift in Fluorocarbon Plasmas**, ***K. Nakamura,*** Chubu University, Japan*; H. Sugai,* Nagoya University, Japan*; K. Oshima, A. Ando, 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 a RF bias to the chamber wall@footnote 1@. This paper reports the effects of the AIB on polymer film deposition onto the chamber walls and the time-variation of radical density in fluorocarbon plasma reactors. 13.56 MHz inductively-coupled plasmas are 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. The AIB drastically suppressed polymer deposition on the biased wall, and the deposition rate decreases by one order of magnitude with ~100 eV ion bombardment compared to the non-bias case. On the other hand, the AIB also reduces a rise time of densities of the fluorocarbon radicals after the discharge starts, and reached to steady state within ~10 s for CF@sub 2@ radicals. @FootnoteText@ @footnote 1@K. Nakamura et al: J. Vac. Sci. Techonol. A 18 (2000) 137.

3:40pm **PS1-MoA6 Etching of Passivated SiO@sub 2@ Film by Fluorocarbon Ions: A Molecular Dynamics Study**, *V. Smirnov, A. Stengatch,* ***V. Pavlovsky***, Sarov Labs., Russia*; S. Rauf, P. Stout, P.L.G. Ventzek,* Freescale Semiconductor

Fluorocarbon plasmas are widely used for etching of dielectric thin films in the microelectronics industry. Fluorocarbon radicals and ions are known to produce a thin passivation layer (~ 2 nm) 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 dielectric etching. Computational molecular dynamics (MD) is one technique that has proven useful for such studies. This paper reports about a MD based investigation of fluorocarbon passivated SiO@sub 2@ film etching by CF@sub x@ (x=1, 2, 3) ions. Our MD code is 3-dimensional and uses the velocity-Verlet method for particle acceleration. Psuodo-potentials for two and three body interactions of Si, O, C, and F have been assembled either using Gaussian based quantum chemistry computations or data available in literature. A variety of fluorocarbon passivation films (with varying thickness and F/C ratio) are prepared by bombarding low to medium energy fluorocarbon ions on SiO@sub 2@. Impact of energetic (50-1000 eV) CF@sub x@ ions on these passivation films is then investigated, and modeling results are used to determine ion etch yield, nature of sputtered clusters, and their energy and angular distributions. Modeling results clearly demonstrate that presence of a fluorocarbon passivation film enhances etch yield compared to a similar but otherwise unpassivated

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

SiO@sub 2@ film. Etch yields peak at an off-normal angle, and SiO@sub x@F@sub y@ constitute the bulk of Si containing sputtered clusters.

4:00pm **PS1-MoA7 Spontaneous Etching of Silicon with F Atoms and XeF@sub 2@: A Unified Model**, ***H.F. Winters***, *D. Humbird, D.B. Graves,* UC Berkeley

A recently proposed molecular dynamics simulation of spontaneous etching of undoped silicon with F has been successful in describing a variety of experimental observations.@super 1@ Insights gained from this simulation (denoted HG) have been used to refine a model which explains other spontaneous etch observations, including etching by XeF@sub 2@ and various effects of doping on spontaneous etching, among others. The model is based on the assumption that the reaction is proportional to the negative ion concentration on the silicon surface (e.g. at SiF@sub 3@@super -@ centers)@super 2@ using the umbrella-type reaction mechanism observed in the simulation. HG predicts a 5 Å SiF@sub x@ layer on silicon exposed to F atoms and it will be demonstrated that XPS data are consistent with this prediction. It will also be shown that XPS data indicate a layer twice as thick (~10 Å) for XeF@sub 2@. Experimental data showing that the layer thickness is relatively independent of incident flux and temperature over significant ranges of these parameters as predicted by HG will be presented. Assuming these layer thicknesses are correct allows us to calculate the negative ion concentration on the silicon surface being etched.@super 2@ These results are correlated with various experiments including reaction probability measurements over the temperature range 200--1000 K and doping experiments with concentrations from ~10@super 15@ to 10@super 20@ dopants/cm@super3@. It will be shown that one model can be used to describe the experimental results for the spontaneous etching of Si(111) by both F and XeF@sub 2@. A plausible explanation will be presented as to why the doping effect in chlorine is large relative to fluorine even though the opposite trend is observed for spontaneous etch rate. Many other experimental results (etch rate proportional to reactant density, insensitivity of product distribution to doping level, etch product composition, and the doping and reaction probability differences between F and XeF@sub 2@) are consistent with this model. Finally, the HG conclusion that etch products are desorbed with significant kinetic energy allows data from modulated beam mass spectrometry calibrated for 300K products to be interpreted properly, leading to determination of the reaction probability from T(surface) = 200 K - 1000 K. The data will be presented and compared with theory. @FootnoteText@@Footnote 1@ David Humbird and David B. Graves, J. Appl. Phys, in press, (2004) @Footnote 2@ H. F. Winters and D. Haarer, Phys.Rev. B, 36. 6613 (1987); 37 ,10379 (1988)

4:20pm **PS1-MoA8 Real-time Spectroscopic Studies of Si Etch Dynamics**, ***A.A.E. Stevens***, *J.J.H. Gielis, M.C.M. van de Sanden, H.C.W. Beijerinck, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Nanometer scale control during IC, MEMS/NEMS and photonic device production becomes more and more an issue. Plasma etching and ion beam processing cause the creation of surface roughness and defects, such as dangling and strained bonds. The roughness and defects resulting from the production process end up at critical interfaces in the devices and, thus, influence their performance in a negative way. Therefore, fundamental studies of the creation of roughness and dangling/strained bonds in plasma and ion beam processing of silicon are required. In the past, mass spectrometry studies in well-characterized beam-etching experiments revealed a great deal of information regarding the synergy between ions and etchant during Si etching. At present, more detailed information is desired and can be obtained with spectroscopic surface diagnostics, which have made significant advances over the last years. Hence, spectroscopic ellipsometry (SE) and second harmonic generation (SHG) are employed in situ and real-time during the etching of Si with beams of Ar@super +@ [10-2000 eV] and XeF@sub 2@. By means of SE the surface roughness is measured. If the etching is dominated by XeF@sub 2@ etching, the surface becomes rough (d@rough@ ~ 1-10 nm). However, when Ar@super +@ ions are driving the etch process, the surface remains relatively smooth (d@rough@ < ~1 nm). Complemented with atomic force microscopy measurements, the dynamic roughness scaling theory, expressed in parameters @alpha@ and @beta@, is applied to find the origin of the roughening processes during the etching. In order to study the creation of dangling and strained bonds SHG studies are being carried out. The role of the ions and etchant in the creation of roughness and defects at etched Si surfaces will be discussed on the basis of the results obtained with these surface-sensitive spectroscopic analysis techniques.

4:40pm **PS1-MoA9 Insights into the Ion Energy Dependence of Ion-Assisted Chemical Etch Rates in High-Density Plasmas**, ***L. Stafford***, *J. Margot,* Universite de Montreal, Canada; *M. Chaker,* INRS-Energie, Canada; *S.J. Pearton,* University of Florida

Over the last few years, important research efforts have been devoted to the development of plasma etching models of various materials in various reactive plasma mixtures. These models generally include a surface kinetic model in which it is usually assumed that the ion-assisted chemical etch rate varies like the square root of the ion energy. This dependence is empirically deduced from the universal energy dependence of physical and ion-assisted chemical etch yields presented by Steinbruchel.@footnote 1@ In the present work, we show from existing experimental data that the ion-assisted chemical etch rate does not necessarily follow this particular energy dependence. A typical example is provided by the etching of ZnO films in an Ar/Cl2 high-density plasma. To explain this behavior, we propose an analytical model in which the formation rate of the adsorbate is assumed to be proportional to the number of adsorption sites. In the specific case of ZnO, the adsorption sites are generated by thermal desorption of oxygen atoms. This is found to induce a non-linear relation between the etch rate and the square root of the ion energy. For oxide materials with more complicated structures like (Pb,Zr)TiO3 (PZT), ion bombardment is required to generate adsorption sites. In this case, the adsorbate formation depends on ion energy, which results in an etch rate that approximately varies like the square root of the ion energy. The predictions of our model are found to be in excellent agreement with the experimental data reported for several materials, for example ZnO, SiO2, HfO2, PZT, PST, and SBT. In addition, the model includes previous ion-assisted etching models such as that developed by Gottscho and his co-workers.@footnote 2@. @FootnoteText@ @footnote 1@ C. Steinbruchel, Appl. Phys. Lett. 55, 1960 (1989)@footnote 2@ R.A. Gottscho, C.W. Jurgensen and D.J. Vitkavage, J. Vac. Sci. Technol. B 10, 2133 (1992) .

5:00pm **PS1-MoA10 A Model of Multilayer Surface Reactions and Simulation of the Feature Profile Evolution in Etching of Silicon in Chlorine Plasmas**, ***Y. Osano***, *K. Ono,* Kyoto University, Japan

A phenomenological model has been made to simulate the feature profile evolution of nanometer-scale etching of Si in Cl@sub 2@. The model incorporates an atomistic picture into the model, to analyse the complex surface reactions in the ion-enhanced etching and investigate their effect to the profile evolution, which involves profile anomalies such as bowing, tapering, and microtrenching. To simulate the reaction process at an atomic scale, we employ a feature profile modeling with two-dimensional array of atomic size cell in the entire computational domain. Monte Carlo calculation of the trajectory and stopping of the incoming Cl@super +@ ion within the surface layers of Si substrate is then performed, on the basis of kinetics of two-body elastic collision. For surface reactions of Cl neutral reactants, we take into account their adsorption on the very surface layer. The removal of Si atom is assumed to be caused by the reaction on the chlorinated surface in terms of this adsorption process Si@sub (s)@+4Cl@sub (s)@ -> SiCl@sub 4(g)@, where (s) and (g) represent the solid and the gas, respectively. Simulation of the feature profile evolution is performed for etching of sub-100 nm patterns. The effect of neutral-to-ion flux ratio is studied in this calculation. The present model illustrates that changes of the flux ratio have a significant effect on surface anomalies, such as sidewall bowing and tapered feature near the bottom, associated with surface chlorination on the feature surface which varies by the flux ratio and the location within the feature pattern.

Plasma Science and Technology
Room 213B - Session PS2-MoA

Emerging Plasma Applications

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **PS2-MoA1 Dielectric Barrier, Atmospheric Pressure Glow Discharges (DB-APGD) : Applications, Diagnostics and Modeling**, ***M.R. Wertheimer***, *I. Radu,* Ecole Polytechnique de Montreal, Canada; *R. Bartnikas,* Hydro Quebec Research Institute, Canada **INVITED**

The field of "cold" (non-equilibrium) plasmas at atmospheric pressure (AP) is receiving much attention, in part due to the reward of more economic processing without vacuum systems. Dielectric barrier discharges (DBD) are a particularly promising subgroup; among these, AP glow discharges (APGD) occur in certain gases with long-lived energetic states, for example in N@sub2@ and in the noble gases. They manifest several remarkable peculiarities, described below, and they have opened application areas as

diverse as (a) polymer surface modification, (b) deposition of novel thin film materials, (c) short wavelength light sources for photochemistry, (d) plasma displays, and numerous others. The presentation commences with a short overview of these recent industrial innovations; we then describe fundamental and applied research on DB-APGD in this laboratory. In the former category, diagnostic and modeling studies in helium are briefly presented : (i) At low applied a.c. voltage, V, a single, multi-µs current pulse per half-cycle occurs, but the "glow" may comprise many geometrically-ordered plasma columns which ignite and extinguish in perfect synchronism; (ii) at higher V, these merge into a "true" APGD, spread uniformly over the entire electrode area. (iii) Under specific conditions of V and the a.c. frequency, f, a "pseudoglow" regime sets in, comprising two or more pulses of monotonically decreasing amplitudes per half-cycle. We explain observations (i) to (iii) and demonstrate excellent agreement between experimental measurements (e.g. spatial and temporal evolution of the discharges) and the two-dimensional theoretical model developed by Novak and Bartnikas. Finally, turning to applied research, the unique capabilities of DB-APGD processing of materials is illustrated with several examples drawn from categories (a), (b) and (c) identified above.

2:40pm **PS2-MoA3 Hot Hollow Cathode Diffuse Arc Deposition of Chromium Nitride Films***, H. Barankova,* ***L. Bardos****, L.-E. Gustavsson,* Uppsala University, Sweden

The hollow cathode in the diffuse arc regime (arc with hot thermionic cathode) was used for deposition of chromium and chromium nitride films. The chromium hollow cathode serving as a gas inlet was connected to a radio frequency (rf) generator with the rf power up to 350 W. The process of generation and performance of the hollow cathode discharge and its transition to the arc regime was examined for different gases. The comparison is also given with other target metals. The reactive process of CrN deposition was investigated. Films were deposited on unheated silicon and steel substrates. Highly oriented crystalline CrN films were deposited at retes up to 4.5 @mu@m/min. The effect of process parameters and their correlation to properties (microcrystalline structure, hardness and deposition rate) of CrN is given.

3:00pm **PS2-MoA4 Atmospheric Plasma Deposition of Abrasion Resistant Coatings on Plastic***,* ***G. Nowling****, M. Moravej, M. Yajima, R.F. Hicks, X. Yang,* University of California, Los Angeles*; S. Babayan,* Surfx Technologies*; W. Hoffman,* Motorola

{The plasma-enhanced chemical vapor deposition of silicon dioxide on plastic has been examined in an atmospheric pressure discharge operating with 2.0 vol.% oxygen in helium, at 100 W RF power, and a gas temperature of ~100@degree@C. Several silicon precursors were studied, including tetramethyldisiloxane (TMDSO), tetramethyl-cyclotetrasiloxane (TMCTS), tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSN). After growth, the thickness, refractive index, composition, and structure of the films were determined by ellipsometry, infrared spectroscopy, and three-dimensional surface imaging. Hardness and abrasion tests were performed as well. Glass films could be deposited at rates up to 1.0 micron/minute using TMDSO. However, these films contained significant amounts of carbon and hydrogen, and abraded easily during scratch tests. Feeding HMDSN to the oxygen plasma resulted in the deposition of SiO@sub2@ films that were free of nitrogen and carbon, contained minimum hydroxyl concentrations, and displayed excellent hardness and scratch resistance at a film thickness >1.5 microns. The maximum deposition rate obtained using HMDSN was 0.3 microns/minute. At the meeting, we will discuss the relationship between the plasma chemistry and the properties of the glass coatings.}

3:20pm **PS2-MoA5 Plasma Surface Modification for In-line Commercial Applications***,* ***A. Yializis****, R.E. Ellwanger,* Sigma Technologies Int'l Inc. **INVITED**

Plasma is the most common state of matter in the visible universe and has been used for decades in commercially important processes. However, such processes have historically tended to be limited to fairly small scale vacuum applications. The idea of using plasma, particularly atmospheric plasma, to add substantial value to a product by modifying the surface of a moving substrate with either added functionality or a thin functional coating is indeed compelling. Emerging applications include elevation of surface energy to promote adhesion or wetability, ablation to remove unwanted residue or material, sterilization, and deposition of a thin functional coating. Sigma Technologies has been at the leading edge of efforts to commercialize these concepts for the past several years and recent results in the aforementioned application areas are presented.

4:00pm **PS2-MoA7 Fundamental Aspects on the Sputter Efficiency in High Power Pulsed Magnetron Sputtering***,* ***U. Helmersson****, J. Alami, J. Böhlmark, M. Lattemann,* Linköping University, Sweden

The use of high power pulsed magnetron sputtering (HPPMS) is an elegant way of producing a large amount of ions from the sputtered materials in magnetron sputtering (MS). HPPMS has great potential in thin film deposition where there is a desire to control direction, lateral distribution, and arrival energy of the depositing species. In this paper we present measurements of the deposition rate using HPPMS and comparing it with normal dc MS. It shows that in general the deposition rate is lower for HPPMS using the same average input power and that the deposition rate scales with the self-sputtering yield of the sputtered material in use. This can be understood in view of the large fraction of ionized metal in the close vicinity of the cathode and that the metal itself will be responsible for a large fraction of the effective sputter ejection of the cathode material. The observed results are also discussed in view of the pulse power and inert gas pressure used.

4:20pm **PS2-MoA8 RF Plasma Deposition of Thin SiO@subx@ Films onto Aluminium Alloy: XPS and Contact Angle Measurements Studies***,* ***A. Azioune****, M. Marcozzi, V. Revello, J.-J. Pireaux,* Lise Namur, Belgium

Protection of (metallic) substrates via paints is widely used in many sectors including the aerospace industry. The efficiency of the process depends on the durability of the paints and on the properties of the interface between the organic layer and the surface metal oxides; thus, the pre-treatment of the aluminium alloy prior painting is a very important step to long term - performance for this technology. However, most of the pre-treatments used now on the aluminium present environmental drawbacks as they are based on solvents and chromates. An alternative efficient and ecologically cleaner method is the plasma technology. In the present work, the aluminium substrates (Al-clad 2024) were cleaned by RF (13.56 MHz) plasma, from a mixture of oxygen and argon gases. It is observed that the carbon contamination is completely removed using Ar plasma. Thin SiO@sub x@ films have been deposited by plasma a mixture of hexamethyldisiloxane (HMDSO) and oxygen (20 W, 5 min). In the absence of oxygen, a thick (> 10 nm) and superhydrophobic (@theta@ @>=@ 100°) film characteristic of PDMS properties is formed; polysiloxane-like thin (< 10 nm) films (SiO@sub x@) are obtained with the introduction of oxygen (20, 50 and 80%). Both XPS and contact angle measurements confirmed both the composition and the structure of these films. More importantly, contact angle measurements using different liquids and interpreted with the van Oss Good Chaudhury theory, allowed to determine the surface free energy of the deposited films: the calculated surface tensions (@gamma@ @subs@, @gamma@ @subs@ @superd@, @gamma@@subs@ @super+@ and @gamma@@subs@ @super-@) of the film formed from HMDSO/O@sub 2@: 50/50 are in excellent agreement with those of reference silicium oxide substrates. @FootnoteText@ This work is supported by Walloon Region (RW n° 021/5208) in the framework of a collective reasearch project "ECOPO" in collaboration with Université de Mons-Hainaut and Coating Research Institute.

4:40pm **PS2-MoA9 Transparent Hybrid Inorganic/Organic Barrier Coatings for Plastic OLED Substrates***,* ***T.W. Kim****,* GE Global Research Center*; M. Schaepkens,* GE Advanced Materials*; M. Yan, A.G. Erlat, M. Pellow, P.A. McConnelee, T.P. Feist, A.R. Duggal,* GE Global Research Center

The use of plastic film substrates enables fabrication of new applications in the area of flexible opto-electronics, such as flexible display and lighting, using low cost roll-to-roll fabrication technologies. One major limitation of bare plastic film substrates in these applications is the rapid oxygen and moisture diffusion through the substrates and subsequent moisture and oxygen induced degradation of the opto-electronic devices. Recently GE has developed a novel coating technology to reduce the moisture permeation rate through the plastic film substrate below 5x10@super-6@g/m@super2@/day using plasma enhanced chemical vapor deposition. Unlike other ultra-high barrier(UHB) coatings comprised of inorganic and organic multilayer, GE's UHB coating comprises a single layer of hybrid inorganic and organic materials. In this single layer, the composition is periodically modulated between silicon oxynitride and silicon oxycarbide. In addition, the transition from one material to the other is continuous, which results in a graded composition structure, so that there is no distinct interface between them. In contrast, other multilayer UHB coatings, where inorganic and organic materials are bound by relatively week van der Waals force, have sharp interface, which sometimes results in delamination of layers especially during the thermal cycle. Hardness and modulus of silicon oxynitride and silicon oxycarbide are tailored such that they are similar to those of typical glasses and thermo plastics, respectively. Modeling studies

suggest that the polymer-like silicon oxycarbide enriched zone decouples the pinhole defects in the silicon oxynitride enriched zone compelling tortuous paths for moisture diffusion, and thus reduces the moisture permeation rate by seven orders of magnitude as compared to that of uncoated plastic substrates. GE's UHB coating also has superior visible light transmittance and color neutrality suitable for the use of display and lighting substrates.

5:00pm **PS2-MoA10 Mass Spectrometric Determination of the Mechanism of the Chemically-Enhanced Reaction of Hydrogen Plasmas and Propellant Surfaces.**, ***R. Blumenthal***, *R. Valliere*, Auburn University

The erosion rate of sprayed-on films of the propellants RDX and HMX under hydrogen plasma exposure are more than one-hundred times the erosion rate in similar argon plasmas. Varying the plasma components impingent on the propellant surface (i.e. ions, radicals, electrons and light) by changing the sample bias and shielding the propellant surface reveals a number of strong synergistic interactions between the individual plasma components in the erosion of the film. Early supersonic pulse, plasma sampling, mass spectrometric studies have indicated that the erosion rate has both a fast and a slow component, but interferences in the mass spectrum have prevented the unambiguous identification of the products, and hence, the chemical mechanism. In this work, the volatile products collected during the erosion of isotopically labeled RDX and HMX will be presented along with a chemical/physical mechanism for the reaction.

Plasma Science and Technology
Room Exhibit Hall B - Session PS-MoP
Poster Session

PS-MoP1 Photoresist Stripping after Low-k Dielectric Layer Pattering Using Axial Magnetic Field Assisted Reactive Ion Etching*, **H.-Y. Song**, C.-W. Kim,* Inha University, South Korea*; J.-K. Yang, C.-W. Lee,* PSK Tech Inc., South Korea*; S.-G. Park,* Inha University, South Korea, Korea, Republic of*; B.-H. O, S.-G. Lee, E.-H. Lee, D.H. Park, G.-J. Kim,* Inha University, South Korea

Effects of axial magnetic field added to the conventional Reactive Ion Etcher(RIE) are studied in terms of plasma characteristics and it is applied to photoresist strip process of dual damascene Cu/low k multi-level interconnection technology. Photoresist remaining on low k dielectric layer should be removed by anisotropic plasma in order to keep vertical profile of low k layers. The magnitude and direction of axial magnetic field can be controlled by the current to a pair of Helmholtz coils. Compared to the conventional RIE, It is found that strip rate is increased by more than 25 % from 1.0 µmm/min and its uniformity is also improved over 300 mm wafers. The effects of axial magnetic field in RIE are also investigated in terms of the selectivity of photoresist over SiOC-H dielectric films and the plasma damage of low k dielectric layers in O@sub 2@/N@sub 2@ plasma. The chemical structures of the low-k SiOC-H film are measured by FTIR spectrometer and the presence of the axial magnetic field is found to suppress any chemical changes of the films while providing wider process window.

PS-MoP2 Etching Characteristics of Organic Polymers by Plasma Beam Irradiation*, **K. Kurihara,*** Toshiba Corp., Japan*; A. Egami, M. Nakamura,* Association of Super-Advanced Electronics Technologies, Japan

Copper interconnection and low-k dielectric interlayer are promising technologies for reducing the RC delay of LSI devices. Organic polymers such as SiLK and GX-3 are one of the candidates of the low dielectric materials. The chemical formulas of these materials have not been clearly opened to the public due to company secrets. It is, therefore, difficult to forecast the characteristics of etching behavior based on the experience. It is important to investigate the relation between the etching behavior and the chemical formulas of organic material for understanding of the fundamental etching mechanisms. In this study, we prepared three kinds of organic films whose compositions were clearly identified. They were methacrylate polymer films, which were polytbutylmethacrylate (PtBuMA), polycyclohexylmethacrylate (PCHMA) and polybenzylmethacrylate (PBMA). The chemical formulas of these films have the same main chain with a different side chain. We investigated the etching characteristics such as etching yield (EY) using a plasma beam irradiation apparatus which can control the plasma parameters precisely. The etch yields of PCHMA and PBMA increased with increase in the ion energy and were saturated over around 330 eV. The etch yield of PtBuMA did not depend on the ion energy above 130 eV. These etch yield behaviors look like the other organic materials such as GX-3 and this can be the notable etching characteristics of organic films. Furthermore we measured desorbed products during nitrogen plasma etching by using a time-of-flight technique. Major desorbed products were HCN and C@sub 2@N@sub 2@ for all organic films we used, and very small amount of C@sub 6@H@sub5@ which is a part of the side chain was also observed in the case of PBMA etching. We will discuss the etching characteristics of organic material based on surface analysis using an in-situ X-ray photoelectron spectroscopy and an energy distribution of the desorbed products. This work was funded by NEDO.

PS-MoP3 Effects of Ar Plasma on DVS-BCB Monomer Used for Low-k Film Deposition*, **T. Wakai**, T. Shirafuji, K. Tachibana,* Kyoto University, Japan

Divinly siloxane bis-benzocyclobutene (DVS-BCB) is an attractive monomer because practical low-k films can be prepared by plasma polymerization of this monomer.@footnote 1@ Recently, its dissociation reaction due to electron impact has been investigated with mass spectroscopy, and fragmentation pattern in the plasma has been discussed by Kinoshita et al.@footnote 2@ However, the DVS-BCB plasma contains excited noble carrier gas and ions, and its effects are not investigated yet. Therefore, we have investigated effects of Ar plasma treatment on DVS-BCB monomer on c-Si with in situ FT-IR reflection absorption spectroscopy. ICP (13.56MHz, 200W) was used for the treatment at room temperature. Duration of the treatment was varied, and temporal change of the spectra was monitored. It has revealed that major reaction due to Ar plasma treatment is opening of benzocyclobutene ring in the monomer. Various bias voltage on the sample was examined during the treatment, which revealed that the ring opening occur even without bias voltage although a few ten eV of plasma potential exists. This means that there are important reaction paths in addition to electron impact dissociation, which can be used for triggering polymerization of DVS-BCB without high energy electrons. Details will be discussed including effects of emission from Ar plasma. This work was supported by NEDO. @FootnoteText@ [1] J. Kawahara et al, Plasma Sources Sci. Technol. 12, S80-S88 (2003). [2] K. Kinoshita et al, Proc. 25th Int. Symp. Dry Process, Nov.13-14, 2003, Tokyo (2003) No.3-01.

PS-MoP4 A New Plasma Source for Destruction of Organic Material in the Post Chamber Hardware, and Implications for Process Endpoint Detection for Specific Low-k Applications.*, **A.K. Srivastava**, P. Sakthivel,* Axcelis Technologies, Inc.*; T.J. Buckley,* Formerly, Axcelis Technologies, Inc.*; A.F. Becknell,* Axcelis Technologies, Inc.

The high temperature ash of photoresist in the presence of certain oxygen-sensitive low k materials requires a plasma discharge devoid of conventional oxidizing agents. In such cases, the chemistries active on the wafer do not entirely destroy the long chain organic polymers that make up the resist. Instead, some of the photoresist is re-deposited on the chamber walls, as well as in the hardware downstream of the wafer. Specifically, parts of the vacuum system comprising the throttle valve, foreline valve and pump lines get coated with organic material, which then have to be manually cleaned during frequent maintenance periods. This leads to significant down time for the ash tool. Due to this oxidizer-free process, there are few emissions in the visible region of the spectrum from reactions at the wafer surface, which makes conventional optical emission based end-point schemes mostly unusable. A compact plasma system has been developed that creates an intense radio frequency (RF) discharge in the exhaust line below the process chamber. Using a secondary inlet for oxidizer agents, the plasma system combusts all incoming organic material before it has a chance to redeposit on the post chamber hardware. Data will be shown on the observed destruction efficiency. Additionally, analysis of the plasma using a residual gas analyzer (RGA), as well as an optical spectrograph to obtain crucial information on the reaction chemistries will be presented. RGA data from diffusion tests show that no oxidizing agent from the downstream inlet makes its way upstream into the chamber where it could potentially harm the low-k material on the wafer. Finally, successful oxidation of the organic material in the plasma source gives rise to optical signals downstream of the chamber that can be used very effectively to extract endpoint for resist removal from the wafer surface.

PS-MoP5 RF-plasma Functionalization of Large Quantity of Carbon Nanotubes: XPS and AFM Analysis of O2 and CF4 Treatments*, **A. Felten**, C. Bittencourt,* LISE, Belgium*; S. Cuenot, R. Daussin, C. Bailly,* Universite Catholique de Louvain, Belgium*; J.-J. Pireaux,* LISE, Belgium

Polymer based electromagnetic screening materials are highly requested nowadays. The fabrication of this material can be achieved by mixing conductive additives to a polymer matrix. CNT are promising ones due to their unique properties. However the formation of homogeneous composite with as grown nanotubes presents a technological difficulty, due to a low compatibility between macromolecules and CNT. To overcome this problem a modification of nanotubes surface by changing their chemical composition was proved to be efficient. There are several ways to modify the CNT surfaces (chemical, plasma@footnote 1@@footnote 2@, fluorination,...). In this work we use inductive RF plasma to functionalize the CNT surface. The nanotubes are Multiwalled prepared by CVD (Nanocyl) and arc discharge (Mercorp). The influence of different plasma conditions (type of gas, power, treatment time, pressure, position of the sample in the discharge) on the functionalization of the CNT was analyzed by XPS. The obtained results show that the concentration of the functional groups bonding at the nanotube surface increased with the treatment time and the plasma power. Concerning the treatment by O2 plasma, the presence of hydroxyl and carboxyl groups has been confirmed by XPS analysis. Depending on the CF4 plasma conditions, it is possible to have either a functionalization of the CNT or a polymerisation of the monomer on the CNT surface. The treatment was scaled up to produce up to 2 grams of nanotubes at once by using magnetic stirring of the powder.An important step of this work was to define the optimal plasma conditions for which the concentration of the fixed functional groups was highest without destruct the nanotube surface. In this way, different plasma treatments were tested on the nanotubes and their surfaces were systematically characterized by atomic force microscopy (AFM).This work is supported by a grant from Region wallone, RW-ENABLE. @FootnoteText@ @footnote 1@H. Bubert et al., Diamond and Related Materials, Vol 12, 3-7,

811-815 (2003)@footnote 2@N. O. V. Plank et al., Applied physics letters, Vol 83, 12, 2426-2428 (2003).

PS-MoP6 Suppression of ArF Photoresist Deformation in Inductively Coupled Plasma (ICP)*, K.J. Lim, **S.-B. Jo**, K.-C. Lee,* INHA University, South Korea*; K.-Y. Jung,* CNI, South Korea*; S.-G. Park,* INHA University, South Korea, Korea, Republic of*; B.-H. O,* INHA University, South Korea

The ArF photoresist, which can be exposed at 193 nm wavelengths, has been applied in semiconductor manufacturing for a 0.1µm feature size and beyond. Recently reported results show that ArF photoresist is much weaker and thinner than KrF (248 nm) photoresist. It will be a challenge in plasma etch process to maintain the integrity of ArF photoresist, leading to be free of resist deformation during critical etch process such as Si@sub3@N@sub4@ hardmask opening. In this paper, plasma etch resistance and morphological changes of ArF photoresist in various plasma etching environments was checked. To determine the main etch parameter causing deformation of ArF photoresist, etching parameters in Inductively Coupled Plasma (ICP) source was varied and compared the results. We present alternative etch techniques consists of a triple sequence of protective layer coating, polymer / photoresist trimming and final etch step. The effect of fluorocarbon layer formation on selectivity and etch profile will be discussed.

PS-MoP7 Experimental Characterization of an Inductively-Coupled Acetylene/Hydrogen Plasma for Carbon Nanofibers Synthesis*, Y.Y. Lin,* National Tsing Hua University, Taiwan*; K.C. Leou,* National Tsing Hua University, Taiwan, ROC*; H.H. Wei, M.T. Wei, **C. Lin**, C.H. Tsai,* National Tsing Hua University, Taiwan

A plasma enhanced chemical vapor deposition process was employed to synthesiz carbon nanofibers on silicon or glass substrates patterened with Ni catalystic films. The plasma was generated by an inductive coil driven by 13.56 MHz RF power with acetylen and hydrogen gas mixtures. The substrates were placed on a temperature controlled staged which was also powered by 13.56 RF voltages. At gas pressure 15-25 mTorr and substrate temperature (surface) 500-600°C, isolated and vertically-aligned carbon nanofibers have been successfully synthesized. This paper reports experimental investigation of plasma properties characterized by optical emission spectroscopy of spectra line intensities of various species such as hydrogen, C@sub 2@ and CH, as well as RF properties at the biased substrate stage measured by RF impedance meter. Measurement results reveal that line intensity of C@sub 2@ increases with acetylene/hydrogen ratio. On the other hand, hydrogen atom density which was estimated by optical actinometry measurements(using Ar as the tracer gas) decreases accordingly. As a consequence, there was more @alpha@-C contents in the nanofibers as verified by both SEM imagies and micro-Ramman measurements. The ion current(or flux) incident on the substrate surface was estimated by the ratio of the RF power over RF voltage amplitudes as measured by the impedance meter. The ion current increased with ICP source power but changed little when the bias power was varied, as expected. The RF voltage amplitude, which is rougly proportional to ion energy, decreased as ICP power was increased. This is because plasma density increases with source power but the bias power is fixed.

PS-MoP8 In-Situ FTIR Characterization of Gas Phase Chemistry in Continuous and Pulsed Inductively Coupled 1,3-Butadiene Discharges in a Gec Cell, Cross-Correlated Against Ex-Situ ATR Surface Analysis*, **A.K. Jindal**,* The University of Texas at Dallas*; A.J. Prengler,* NEC*; J.R. Frautschi,* Western Life Sciences*; L.J. Overzet, M.J. Goeckner,* The University of Texas at Dallas

Gas-phase chemistry of 1,3-Butadiene plasmas and resulting deposited film chemistries are examined. In-situ Fourier Transform Infrared Spectroscopic (FTIR) diagnostics are used to characterize the chemistry at 50 mTorr pressure in continuous and pulsed regimes of the discharge, in an inductively coupled gaseous electronics conference cell. The continuous discharge was examined using a designed experiment with pressure, power, and gas flow being the free parameters. The pulsed discharge was examined at duty cycles ranging from 87 to 3 percent, all acquired at 50 mTorr, 8 sccm, and 60 W (during plasma "on" phase). When the plasma was pulsed with a 50 percent duty, approximately 10 percent of the polymer was broken apart. This increased to approximately 20 percent for the continuous discharge. Ex-situ Attenuated Total Reflectance (ATR) diagnostics are used to study the surface chemistry resulting from plasma deposition of Butadiene on bare silicon substrates under both continuous and pulsed regimes of the discharge, restricted to the same conditions presented above. Surface analysis in the pulsed modes was performed for each individual duty cycle, along with analysis of film grown using combined cycles. FTIR data is cross-correlated against the ATR data to better understand the interactions between plasma induced gas phase and surface chemistry. This work is supported in part by grants from NSF/DOE, CTS-0078669 and NSF, CTS-0079783.

PS-MoP9 Impact of Plasma Polymerization on Cd Bias and Ler*, **S.K. kim**,* Cypress Semiconductor, usa

CD bias and LER are the most critical factors to enable sub-90nm technology contact hole formation in terms of good Rs and barrier deposition. As pattern density increases, ARC (Anti-Reflective-Coating) layer is essential together with 193nm resist to print good contact holes. It, however, drives plasma contact etch much more challenging than before because ARC material is similar to PR(Photo Resist) and during the ARC plasma etch PR degradation is inevitable. In addition, oxide etch chemistry is evolving to create more carbon rich polymers for 193nm resist selectivity and is getting O2 gas dependant to control the amount of the polymer, which caused LER worse. In this study, impact of plasma polymerization during the plasma oxide etching on CD bias/LER was evaluated. Polymerization can be dominated by etching gas combination. Adding Freon 134(C2H2F4) into conventional ARCE chemistry such as CF4/CHF3 and oxide etch(C4F6/O2) enables to modulate CD bias/LER. Local non-uniformity of oxygen atoms in the contact hole is the root cause of LER. Etching sequence, adding dry CLN step at the end of oxide etch step is also play an important role on CD bias/LER as well. Furthermore, Impact of process parameters such as CF4/CHF3 ratio and etching time will be discussed.

PS-MoP10 Deformation of ArF Photoresist and Silicon Nitride Etching using Dual Frequency Superimposed (DFS) rf Capacitive Coupled Plasma*, **D.H. Kim**, S.H. Cho, J.G. Lee, N.-E. Lee,* Sungkyunkwan University, South 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 unpatterend ArF photoresists by varying the process parameters such as HF(13.56, 27.12, and 60 MHz)/LF(2 MHz) power ratio, pressure and etch chemistry (CHF@sub3@/CF@sub4@/CH@sub2@F@sub2@/Ar/O@sub2@/N@sub2 @). Characterization of surface chemical change was performed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Surface morphological changes also investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Also, morphological changes of surface and line edges in ArF PR, SiN etch rate, selectivity over PR during etching of ArF PR/BARC/SiN structures were investigated. The results indicated an increased deformation by increasing the low frequency power and flow rate of Ar and O@sub2@. Effects of process parameters on the etch results will be discussed in detail.

PS-MoP11 Si@sub x@O@sub y@F@sub y@ Passivation Layer in the Silicon Deep Etching Cryogenic Process*, **X.M. Mellhaoui**, R.D. Dussart, T.T. Tillocher, **P.L. Lefaucheux**, P.R. Ranson,* GREMI - Orléans University, France

Silicon etching is perfomed by a cryogenic SF@sub 6@/O@sub 2@ plasma process. This process allows to obtain a high aspect ratio (depth/width > 10) and a high anisotropy. The plasma is created in an Inductively Coupled Plasma reactor (Alcatel 601E). The silicon wafer is clamped on a electrostatic chuck cooled with liquid nitrogen and controlled in temperature with thermal resistances. A study of passivation mechanisms is necessary to perfectly control this process and to optimize the trench profiles. The passivating layer is a mixture of Si, F, O (Si@sub x@O@sub y@F@sub z@). Previous XPS experiments have shown that the passivation layer is removed during the increase of temperature. When destroyed, this layer can be rebuilt with a plasma mixture of SiF@sub 4@ and O@sub 2@. This particular experiment was made and has revealed that the presence of sulphur is not necessary to build an efficient passivation layer. In new experimental ICP reactor was equipped with a spectroscopic ellipsometer. This new diagnostic allowed to characterize the kinetic of passivation layer growing in the cryoetching process, and it desorption when the wafer is

warmed. Mass spectrometry experiments were also carried to analyze the desorbed species These new results will be presented at the conference.

PS-MoP12 High Aspect Ratio Contact Hole Etching in C@sub 4@/F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ and c-C@sub 4@/F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ Plasmas, *H.-K. Ryu,* LG Chem, Ltd., Korea*; **C.B. Shin,*** Ajou University, Korea*; Y.-W. Kim,* Hynix Semiconductor, Inc., Korea*; C.-K. Kim,* Ajou University, Korea

A high aspect ratio contact hole etching of dielectrics (e.g., SiO@sub 2@) is one of the key processes in developing the next generation ultra large scale integrated devices because of the rapid shrinkage of the design rule to the nanometer level. To meet the several requirements for a high aspect ratio contact hole etching, a high etch selectivity to mask (e.g., photo resist) is practically required to maintain the critical dimension (CD) of the small-size contact hole. Also, bowing-free structures are needed for the etched profiles. Perfluorocarbons (PFCs) such as c-C@sub 4@F@sub 8@ are widely used as etchant gases for contact hole etching. These PFCs, however, are considered to be problematic from an environmental point of view because of their long atmospheric lifetimes and high global warming potentials (GWP). Several classes of environmentally benign chemistries have been examined as alternatives to PFCs and unsaturated fluorocarbons (UFCs) are one of the attractive candidates due to their shorter atmospheric lifetimes and lower GWP. In this study, we reports on an etching of a SiO@sub 2@ contact hole with a diameter of 0.17 µm and an aspect ratio of 15 using C@sub 4@F@sub 6@/O@sub 2@/Ar and C@sub 4@F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasmas (UFC-containing plasmas). It was shown that the addition of CH@sub 2@F@sub 2@ gas made the CD of the contact hole to be maintained, reduced the degree of bowing, and enhanced the etch selectivity to photo resist during a high aspect ratio contact hole etching in a C@sub 4@F@sub 6@/O@sub 2@/Ar plasma. A SiO@sub 2@ contact hole etching in a c-C@sub 4@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasma (PFC-containing plasma) was also conducted to compare the etch profiles and contact resistances obtained in the two different gas discharges: C@sub 4@F@sub 6@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ and c-C@sub 4@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasmas.

PS-MoP13 Investigation on the Plasma Parameters and the Properties of the Reactively Sputtered Titanium Oxynitride Thin Films*, **A. Karuppasamy**, A. Subrahmanyam,* Indian Institute of Technology Madras, India

The titanium oxynitride thin films were prepared by reactive dc magnetron sputtering of metallic titanium using a gas mixture of argon, oxygen, and nitrogen. The Argon and nitrogen flow rates were kept constant while the oxygen flow rate was varied .The target was sputtered with a constant current density of 90 Am @super-2@. The films were deposited on quartz and glass substrates, kept at a constant temperature of 573K. The in situ plasma discharge diagnostics were done by optical emission spectroscopy(OES)and Langmuir probe.The emission signal was detected by a miniature fiber optic spectrometer (Ocean Optics SD 2000) coupled with a quartz fiber in the spectral region from 350 nm to 850 nm. Emission lines of different species of titanium, nitrogen and oxygen were analyzed. The plasma parameters like the plasma potential, electron temperatures, plasma density and the ion energy distribution function (IEDF) were measured using Langmuir probe. The crystallographic structure and composition were examined by X-ray diffraction (XRD) and RBS.The temperature dependent electrical conductivity measurements in the range 10 K to 300 K shows an increase in the activation energy with increase in the oxygen content of the films. The index of refraction, extinction coefficient and thickness of the films were measured using a phase modulated spectroscopic ellipsometer in the energy range 1.65 - 3.1 eV. The transparent films were analyzed with Sellmeier dispersion relation while the semi-transparent films with Cauchy polynomial function. With increase in the oxygen flow rate, a sharp increase in the refractive index is observed. The optical transmittance spectra of the films were measured in the energy range 0.56 to 5.61 eV.The carrier concentration and mobility were estimated by low temperature(10 K) Hall measurements.Work function of the films were measured by contact potential method using the kelvin probe.The plasma conditions required for a high quality film will be discussed.

PS-MoP14 Anomalous Ionization of Copper Atoms in Argon-Based Sputtering Plasmas*, **H. Kadota**, K. Nakamura,* Chubu University, Japan*; N. Nafarizal, K. Sasaki,* Nagoya University, Japan*; M. Kobayashi,* ANELVA, Japan

Plasma-enhanced metal sputter deposition has been widely used for formation of seed and/or barrier layers of high aspect ratio contact holes in ULSI semiconductor devices. In this process, sputtered metal atoms are ionized during flight in Ar plasma, and the metal ions can arrive at the bottom of the hole since the metal ions are accelerated in the sheath around the wafer in the direction perpendicular to the substrate. This paper reports on ionization characteristics of sputtered copper atoms in Ar plasmas, especially for ionization fraction of the copper atoms as well as ion density ratio of copper to argon. An inductively-coupled argon plasma is produced in a stainless steel vessel by supplying 13.56 MHz RF powers with a loop bare copper antenna. A blocking capacitor is inserted in series at each end of the antenna conductor, consequently a negative self-bias voltage appears during the operation at the antenna. Therefore, copper atoms are injected into the plasma because of physical antenna sputtering. The ion density ratio [Cu@super +@]/[Ar@super +@] is obtained by combining mass spectroscopic measurements and Langmuir probe measurements, whereas the copper ionization fraction is measured with a biased crystal micro balance. The ion density ratio increases with the Ar pressure, and reaches ~30 at ~100 mTorr. The ionization fraction also increases with the Ar pressure and approximately reaches ~100% at the same pressure. This means that copper plasma is likely to be produced even in the argon discharge. These characteristics are independent to the discharge power, suggesting an ionization mechanism of the copper atoms except for electron impact.

PS-MoP15 Ionization Processes of Metal Atoms in High-Pressure dc Magnetron Sputtering Discharges*, **N. Nafarizal,*** Nagoya University, Japan*; K. Shibagaki,* Suzuka National College of Technology, Japan*; N. Takada,* Nagoya University, Japan*; K. Nakamura,* Chubu University, Japan*; M. Kobayashi,* ANELVA Corporation, Japan*; K. Sasaki,* Nagoya University, Japan

Ionized physical vapor deposition (IPVD) is a key technology in the formation of seed and/or barrier layers on the surfaces of trenches and holes with high aspect ratios. In IPVD, metal atoms sputtered from the target are ionized in the gas-phase, and metal ions are accelerated toward the biased wafer by the sheath electric field. To optimize this technique, it is necessary to know ionization processes of metal atoms. In the present work, we measured the density distributions of Ti and Ti@super +@ in dc magnetron discharges by laser-induced fluorescence imaging spectroscopy. We observed significant production of Ti@super +@ in the gas phase in high-pressure (@>=@100 mTorr) discharges. The distribution of the Ti@super +@ density had a peak at a distance of 5-6 cm from the target surface. Namely, the production of Ti@super +@ was obtained in dark plasma with a low electron temperature, and was not obtained in bright region near the target with a high electron temperature, indicating that electron impact ionization of Ti is not the production process of Ti@super +@. As another possible candidate of the production process of Ti@super +@, we investigated Penning ionization (collision between Ti and Ar@super M@) by measuring the density distribution of Ar at a metastable state (Ar@super M@). In addition, we estimated the density ratio between Ti@super +@ and Ar@super +@ from the total plasma density measured using a Langmuir probe. The result suggests that Ti@super +@ is the dominant ion in the down flow region of the high-pressure discharge.

PS-MoP16 Plasma Chemistry of a Nb/Ar/O@sub 2@ Magnetron Discharge*, **S. Mráz**, M. Wuttig, J.M. Schneider,* RWTH Aachen, Germany

We have investigated the plasma chemistry of a DC reactive magnetron discharge with a mass energy analyser. We have studied the effect of the oxygen partial pressure on the positive and negative ion populations of the discharge. The current supplied to the magnetron and the total pressure were kept constant throughout the experiments at 900 mA and 0.8 Pa, respectively. The plasma chemistry is strongly affected by the oxygen partial pressure. As the oxygen partial pressure is increased the formation of oxygen based positive and negative ions is observed. Furthermore, we present evidence for the oxygen partial pressure dependent presence of NbO based clusters, both positively and negatively charged. As the oxygen partial pressure is increased the NbO based clusters become the dominating Nb based ionic species in the plasma. These findings are of relevance for the chemical composition and structure evolution of thin NbO@sub x@ films.

PS-MoP17 Dry Etching of (Pb,Sr)TiO@sub 3@ Thin Films Using Inductively Coupled Plasma*, **C.I. Kim**, K.T. Kim, G.H. Kim,* Chungang University, Korea*; T.H. Kim,* YeoJoo Institute of Technology, Korea*; C.I. Lee,* Ansan College of Technology, Korea

Recently, ferroelectric thin films have received great attention for the application to high density memory devices. Among the various ferroelectric films, the BST thin film was noticed as the most promising material due to its high dielectric constant and paraelectricity at normal operating temperature. Although BST possesses a satisfactorily high dielectric constant, 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. Strontium titanate (SrTiO@sub 3@) is one of the few titanates which is cubic at room temperature. But, the dielectric constant is lower than BST. The addition of lead into strontium titanate makes its dielectric constant(1377) higher and the temperature of crystallization lower. Therefore, (Pb,Sr)TiO@sub 3@ (PST) thin film can be a promising material due to its high dielectric constant and paraelectricity at normal operating temperature. However, there is no report on the characteristics and mechanism of PST thin films during etching process. In this study, inductively coupled plasma etching system was used for etching PST because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of PST thin films were investigated in terms of etch rates and selectivity as a function of gas mixing ratio, rf power, dc bias voltage and chamber pressure. The BCl@sub 3@/Cl@sub 2@/Ar plasmas were characterized by optical emission spectroscopy (OES), quadruple mass spectrometry (QMS) and Langmuir probe analysis. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-MoP18 Irregular Pattern Deformation in Etching of High Aspect Ratio Contact Holes*, **S.-I. Cho**, S.-Y. Son, Y.-J. Kim, M.-C. Kim, K.-K. Chi, C.-J. Kang, J.-T. Moon,* Samsung Electronics Co. LTD, South Korea

During the high aspect ratio etching process, the transferred pattern may be distorted by the deflection of ion trajectories due to the local charge build-up and nonuniform polymer deposition. The integrity of devices increases, high aspect ratio structures are required to meet the device architecture. Top-down shapes of the etched profiles are observed at various depths of contact holes with high aspect ratio. The top-down shapes are distorted and become irregular as the depth becomes deeper than the aspect ratio of 10. The degree of the pattern deformation is monitored at various process conditions using the contact holes with the aspect ratio of 17. The degree of the pattern deformation is changed with the process parameters, such as C/F ratio, residence time, bias energy, and frequency. We also investigate the correlation of the deformation with the radical species, bias energy, plasma density, and bias frequency by analyzing optical emission spectroscopy (OES), plasma potential, and auger electron spectroscopy (AES). The result of OES shows that the etched pattern becomes more severely distorted when the larger CF2 radicals exist in the gas phase. The profile deformation is not only controlled by polymer species but also by ion energy. The pattern distortion becomes worse by lowering ion energy. Based on results, irregular pattern transfer in high aspect ratio contact holes is caused by nonuniform polymer deposition and the deflection of ion trajectory due to the local charge build-up.

PS-MoP19 Etching Profile of (Ba,Sr)TiO@sub 3@ Thin Films in a BCl@sub 3@/Cl@sub 2@/Ar Inductively Coupled Plasma*, C.I. Kim, K.T. Kim, **G.H. Kim**,* Chungang University, Korea

(Ba@sub 1-x@,Sr@sub x@)TiO@sub 3@ (BST) thin film attracts a great interest as a new dielectric material in capacitors for the next generation ultra-large scale integrated dynamic random access memories (ULSI DRAMs), such as giga bit DRAM in the wide range of research institutes to semiconductor industries because of its large dielectric constant, low leakage current and low dielectric loss. In order to realize the higher integration, it is important to minimize the dimension of storage capacitors, simplify the memory cell structure and maintain sufficient accumulated electric charge within a smaller capacitor. Although BST thin films are excellent capacitor dielectric materials for DRAMs, there are several problems such as fine pattern transfer and no plasma induced-damage etc. In order to solve these problems, the etch behavior of BST with BCl@sub 3@/Cl@sub 2@/Ar gas mixtures is performed with inductively coupled plasma (ICP). In this study, inductively coupled plasma etching system was used for BST etching because of its high plasma density, low process pressure and easy control bias power. The etching characteristics of BST thin films were investigated in terms of etch rates and selectivity as a function of Cl@sub 2@/Ar and additive BCl@sub 3@ into Cl@sub 2@/Ar, rf power, dc bias voltage and chamber pressure. The Cl@sub 2@/Ar and additive BCl@sub 3@ into Cl@sub 2@/Ar plasmas were characterized by optical emission spectroscopy (OES), Langmuir probe analysis and quadruple mass spectrometry (QMS). In order to minimize the pattern transfer difference between a dense cell pattern and isolated pattern, we investigated the effects of process parameters (rf power, dc bias, process pressure and residence time) in Cl@sub 2@-based ICP etching. Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-MoP20 Characteristics of Neutral Beam Generated by 3-grid Low Angle Forward Reflected Neutral Beam System and its Etching Properties*, **D.H. Lee**, B.J. Park,* Sungkyunkwan University, South Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea

Plasma etching is widely used for the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage resulting in physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is to use low energy neutral beam. In fact, many studies have been conducted previously and currently being conducted to generate parallel and low energy neutral beams and to etch materials vertically without having electrical charging and physical damage. In our study, to extract the parallel neutrals from the plasma, a neutralizing reflector having less than 5 degree sloped to the extracted ions was used which called low angle forward reflected neutral beam. In this study, the characteristics of a neutral beam and the etch characteristics of Si and SiO2 for SF6 gas have been studied using a low-angle forward-reflected neutral (LAFRN) beam system. In other to obtain higher neutral flux and lower beam energy, a 3-grid system was used to the neutral beam source and the neutral beam energy and flux was investigated using a quadrupole mass spectrometer.

PS-MoP21 Plasma Etching of Pyrex Glass by Inductively Coupled Plasma for Fabrication of Microfluidic Channel*, **J.H. Park**, N.-E. Lee,* Sungkyunkwan University, South Korea*; J.S. Park, H.D. Park,* Korea Electronics Technology Institute, South Korea

Among many micromachining technologies of glass for microfluidic channel fabrication, DRIE (deep reactive ion etching) has been becoming increasingly attractive because of the trend towards micrometer-scale and nanometer-scale pattern in the glass or quartz. However, low etch rate of glass during plasma etch has limited the usefulness of plasma etch in the fabrication of high aspect ratio structure of glass @footnote1-3@. In this study, DRIE of pyrex glass was carried out using SF @sub 6@-based gas chemistry in a commercial 8â?• inductively coupled plasma (ICP) reactor (TCP 9100, Lam Research Corp.). The glass substrate used in this experiment was pyrex glass with the thickness of 700 µm and 1cmï,´1cm squared-shape. As a etch hard-mask, Ni was electroplated into patterned SU-8 photoresist mask with the line and spacing pattern of 12-15µm on Cu /Cr /glass structure. In case of using SF @sub 6@ only, edge profiles of glass showed under-cutting below the Ni hard mask due to chemical etching and trenching or cusping at the bottom of etched channel occurred. Etch rate of @<=@0.75µm/min was obtained. On the other hand, in case of using SF @sub 6@/Ar chemistry, profile improvement without under-cutting and trenching phenomena was observed compared to the case of SF @sub 6@ chemistry but etch rate was slightly decreased. Etch rate of @<=@0.54µm/min was obtained. Ar addition was effective in the removal of etch residues by high-flux Ar ion bombardment leading to improved profile and removal of bottom trenching. XPS results indicate that sputtering etching helps remove nonvolatile by-products such as AlF@sub3@, NaF, and BF. In case of SF @sub 6@ /C @sub 4@F@sub 8@/Ar chemistry, etch characteristics of pyrex glass were similar to those of SF @sub 6@ and SF @sub 6@ /Ar chemistries but glass etch rate was slightly increased. Optimized process showed the following performance: angle profile: >88°, and glass etch rate: 0.8µm/min.

PS-MoP22 Etching Characteristics of Al-doped ZnO Thin Films in ICP Etcher*, **S.W. Na**, M.H Shin, Y.M. Chung, J.G. Han, J.-H. Boo, N.-E. Lee,* Sungkyunkwan University, South Korea

Recently, the greatly increasing use of transparent conducting oxide (TCO) films such as indium tin oxide (ITO) for flat panel displays has promoted the development of inexpensive TCO materials including Al-doped ZnO (AZO).

AZO films have high electrical conductivities as well as high optical transparencies. From the manufacturing viewpoint, TCO films should be easily etched in order to fabricate fine electrodes. Therefore, dry etch characteristics of ZnO and Al-doped ZnO films need to be investigated. In this study, etching characteristics of AZO thin films using inductively coupled plasma (ICP) etcher. AZO thin films with thickness of 300~400nm and different Al doping concentrations were prepared on wafer substrates by RF magnetron sputtering and photolithographic patterning of a positive photoresist mask (AZ7220) was followed. An rf power of 13.56MHz was applied to the top electrode coil to induce ICP. Bottom electrode power of 13.56MHz was applied to the substrate holder to induce self-bias voltage to the wafer. Plasma etching of AZO thin films was investigated by varying gas mixing ratio of Cl@sub2@/(Cl@sub2@+Ar) and CH@sub4@/(CH@sub4@+Cl@sub2@+Ar) chemistries, top electrode power, and bottom electrode power. Etch rate and profiles on different weight percent of AZO thin films were measured by the scanning electron microscopy (SEM). In order to understand the etching mechanism, optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) are used to investigate the chemical states of the etched surface with various gas mixing ratios. The etch rate was increased with increasing rf bottom power and top electrode power and the etch rate of >= 200 nm/min was achieved. From the various measurements, it was found that the addition of Cl@sub2@ and CH@sub4@ gases plays an important role in determining the etch arte. Etching characteristics of AZO films with different Al doping concentrations will be discussed in detail.

PS-MoP23 Effect of BCl3 Addition on Etching Characteristics of TaN in BCl3/Cl2/Ar Inductively Coupled Plasma*, M.H Shin, S.W. Na, N.-E. Lee,* Sungkyunkwan University, South Korea*; J.H. Ahn,* Hanyang University, South Korea

Patterning of absorbers is a crucial step in the manufacturing of EUVL (Extreme ultra-violet lithography) masks due to the stringent CD and reflectance requirements. So, patterning characteristics of new absorber materials for EUVL masks have to be evaluated [1]. Tantalum nitride (TaN) is one of the candidates for absorber layers in the mask used for the next generation EUVL and X-ray lithography because of the relative ease of patterning and its durability in cleaning processes. In this work, etching characteristics of 500-nm-thick TaN layers were investigated in a modified 8 inch commercial ICP (inductively coupled plasma) etcher having a 3.5 turn spiral copper coil on the top of chamber separated by a 1-cm-thick quartz window. RF powers of 13.56MHz were applied to the top electrode coil and the substrate holder to induce ICP and self-bias voltage to the wafer, respectively. In order to investigate the effect of BCl@sub 3@ addition to Ar/Cl@sub 2@ chemistry on the TaN etch characteristics, TaN etch rates were measured by changing the added BCl@sub3@ flow rate and the bottom electrode power while the Cl@sub 2@ and Ar gas flows are fixed at 80sccm and 20sccm, respectively. To understand the role of BCl@sub 3@ gas in BCl@sub 3@/Cl@sub 2@/Ar ICP etching, the relative change in the densities of Cl and Ar radicals and the chemical binding states of etched TaN surfaces were measured by optical spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS), respectively. The results showed the relative density of the Cl radicals was higher in the BCl@sub 3@/Cl@sub 2@/Ar chemistry than in Cl@sub 2@/Ar chemistry at the same total gas flow rate. The effects of BCl@sub 3@ addition to Cl@sub 2@/Ar chemistry on the etch characteristics of TaN (etch rate, selectivity over SiO@sub 2@ buffer layer, etc) will be discussed in detail. [1] F. Letzkus, J Butschke, M. Irmscher, F. M. Kamn, C. Koepernik, J. Mathuni, J. Rau, G. Ruhl: Microelectronic Engineering 2004.

PS-MoP24 High-density Plasma in Low-pressure will Cast a Bright Foresight in a 45 nm Node Etching Process*, Y. Morikawa,* ***T. Hayashi****, K. Suu, M. Ishikawa,* ULVAC, Inc., Japan

For the next-generation lithography, whose target dimensions are below the 100 nm realm, ArF lithography is considered to be a promising technique. However, an ArF resist has poor etching resistance, which brings on low mask selectivity and results in striation or pitting by resist degradation. This is a serious problem in a future device fabrication. We have studied etching characteristics of organic materials in view of pressure dependence and relations of etching species. Obtained results suggest organic materials are very reactive with atomic hydrogen, oxygen, halogen and other molecular radicals, and therefore, high density plasma in low pressure below 1 Pa is very useful to achieve anisotropic etching of organic films and porous dielectric materials with ArF resist mask without striation. Organic materials including ArF resist may react with radicals, so chemical / physical properties of the organic films may change and resulting degradation may occur under the energetic particle irradiation in the etching plasma. An important issue in the porous low-k etching process is the film damage(ref.1) (degradation of the etched sidewall). If the thick sidewall protective film is formed, this damage may be suppressed. However, it is necessitated that a thin protective film is formed on the sidewall in the finely patterned holes and lines below 100 nm. Nitrogen additive plasma may answer this problem. Under a certain etching condition, it was deduced that the protective thin film formed in the nitrogen additive plasma was composed by some kinds of fluorinated acrylonitrile polymer. 1) Y. Morikawa, N. Mizutani, M. Ozawa, T. Hayashi, W. Chen, and T. Uchida, J. Vac. Sci. Technol., B 21 (2003) 1334.

PS-MoP25 Study on Effects of Ion Irradiation on Plasma Anisotropic Cu CVD using a Triode Discharge*,* ***K. Takenaka****, T. Kaji, K. Koga, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Plasma anisotropic CVD method can realize bottom-up filling of Cu in a trench without sidewall deposition. @footnote 1,2@ This method is promising for Cu metallization in ULSI, since it has a potential to fill extremely narrow trenches and holes with a high aspect ratio. In order to reveal the anisotropic deposition mechanism, we have studied the deposition profile on a Si substrate with trenches using a triode discharge, for which a grounded mesh is placed at 10 mm above the substrate to control flux of ions impinging on the substrate. Without ion irradiation, nothing is deposited on the top, bottom and sidewall. With irradiation of ions of a low energy below 12 eV, the deposition rate on the top is 2 nm/min; while that on the sidewall increases with a trench width W from 0 nm/min for W @<=@ 1500 nm to 0.25 nm/min for W = 3300 nm, and the deposition rate on the bottom increases with W from 0 nm/min for W @<=@ 700 nm to 0.9 nm/min for W = 3300 nm. These results suggest the following three items; 1) ion irradiation is necessary for the deposition, 2) low energy ions are hard to reach the bottom of a narrow trench, 3) a fraction of low energy ions impinge on the sidewall of a wide trench. The items of 2) and 3) indicate that a width and an aspect ratio of trench have an influence on kinetic energy and flux of ions reaching bottom and sidewall. Based on the results, effects of ion irradiation on the plasma anisotropic CVD will be discussed in the presentation. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Mater. Sci. Semicond. Proc. 5 (2003) 301.@footnote 2@ K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) in press.

PS-MoP26 Deep Silicon Etch and In-Situ Passivation of Silicon Mold*,* ***S.-B. Jo****, S.-G. Lee, E.-H. Lee,* INHA University, South Korea*; S.-G. Park,* INHA University, South Korea, Korea, Republic of*; B.-H. O,* INHA University, South Korea

Silicon mold is attractive for polymer embossing applications, since the properties of silicon and micro-machining process have been highly characterized through the integrated circuit fabrication. In this article, we present modified Bosch process to obtain high aspect ratio silicon mold with conventional Inductively Coupled Plasma (ICP), without the need of expensive Bosch process systems. In modified Bosch process scheme, silicon etch / sidewall passivation time is much longer than commercialized Bosch process systems and process transition time was introduced between silicon etch and sidewall passivation. Etch profile is significantly varied with external parameters, such as silicon etch / sidewall passivation time, ion energy, and substrate temperature. The variation of fuorocarbon film properties was characterized for various process parameters. Deeply etched micro-structure on silicon mold was well transferred to polydimethylsiloxane (PDMS) and may be suitable for polymer embossing applications.

PS-MoP27 Instabilities of Nanoporous Silica (NPS) During Plasma-Based Pattern Transfer and Subsequent Resist Stripping*,* ***X. Hua****, T. Kwon, R. Phaneuf,* University of Maryland, College Park*; G. Oehrlein,* University of Maryland, College Park, US*; P. Lazzeri, M. Anderle,* ITC-irst, Italy*; P. Jiang,* Texas Instruments, Inc.*; C.K. Inoki, T.S. Kuan,* University at Albany, SUNY

We have investigated several instabilities of nanoporous silica associated with the fluorocarbon plasma-based transfer of resist masks and subsequent removal of the resist mask. Novel phenomena that are absent during plasma exposure of a homogeneous material, e.g. SiO@sub 2@, are observed for NPS materials as a result of the changes in the plasma surface interactions. These include changes in the morphology of near surface pores along with plasma-process dependent surface roughening of the NPS etching front. The instabilities are dependent on of both the plasma properties and NPS characteristics, e.g. overall porosity. The physical mechanisms giving rise to these instabilities in fluorocarbon-based plasma will be discussed based on plasma and surface characterization results. Resist mask removal can lead to deep modifications of NPS materials, e.g.

carbon loss and an increased dielectric constant. We have investigated the potential of direct and remote plasmas fed with N@sub 2@/H@sub 2@/O@sub 2@ precursor gas mixtures and substrate temperature to maximize resist removal rate while minimizing NPS materials modifications.

PS-MoP28 Real-Time Etch Optimization in Electron Cyclotron Resonance-Microwave CO/H@sub 2@ and CO@sub 2@/H@sub 2@ Plasmas*, **A.A. Dyachenko**, A.S. Orland,* Auburn University*; R. Blumenthal,* Auburn Univerisity

Previous results, in our group@super 1@, have indicated that the etch rates of nickel are significantly enhanced when formic acid appears in CO/H@sub 2@ plasmas and when oxalates appear in CO@sub 2@/H@sub 2@ plasmas. At that point, it was not clear whether the formic acid and oxalates are new primary etchants or daughter ions of the metal complex product. In this work, a real-time monitoring of the concentrations of chemically generated species in electron cyclotron resonance (ECR) hydrogen plasmas is investigated by means of supersonic pulse plasma sample mass spectrometry. The influence of various plasma parameters, on the concentration of etching products/etchants and on the actual etch rates, has been examined with a -200 V DC bias at maximum brightness. Above 30% CO concentration, contamination of the vacuum chamber occurs and therefore experiments under such conditions have not been conducted. Upon decreasing the CO fraction from 30% to 5%, an increase on the order of 30% in the formic acid concentration was observed. Increasing microwave power from 150 W to 250 W results in a 20% increase in the formic acid concentration. Correlations and anticorrelations between the concentrations of reactive species formed in the plasma and the etch rates measured by profilometry will be presented along with a chemical mechanism consistent with the observed etch rate enhancement. Similar results for oxalates in CO@sub 2@/H@sub 2@ plasma will also be presented. @FootnoteText@ @footnote 1@ A.Orland, Ph.D. thesis, Auburn University, 2003.

PS-MoP29 Anisotropic Etching of Sio@sub 2@ Film and Quartz Plate Employing Anhydrous Hf*, **T. Fukasawa,*** Tokai University, Japan

Plasma etching technology has been widely used since the 1980s in the fabrication of ultra-large-scale integrated (ULSI) circuits. However, charged particles such as ions and electrons generate ion implantation to Si, have charge up damage to SiO@sub 2@ film and have low selectivity of the photoresist. On the other hand, HF gas is also widely used in a removal process of native SiO@sub 2@ films and in a cleaning process of a wafer as a dry process. Only chemical reactions are dominant in the reactions of HF gas etching and Si is not etched by HF gas, consequently, non-damaged, highly selective etchings of SiO@sub 2@ film and quartz plate can be achieved in HF gas etching. However, almost all reports about HF gas etching were isotropic etchings. When I investigated planarization technology employing anhydrous HF gas, very unique etching characteristics were observed when the etched depth of AHF gas etching was measured employing OFPR-800 as a photoresist. The stage temperature was set at 20° C and AHF gas was introduced to the chamber at a pressure of 30 Torr. After 15 min etching, AHF gas selectively etched the quartz surface just below the OFPR resist. In this etching, neither plasma nor ultraviolet light was used. A SiO@sub 2@ film below the photoresist, OFPR-800, was selectively etched with AHF gas. However, etch-stop was observed at the depth of 1.5 µm after 15 min. I found that the flow rate of HF gas and a high-pressure process were very effective with regard to this issue. When the flow rate of HF gas was increased to 4300 sccm, etching never stopped over 40 min and 20 µm in depth. The etched depth increased linearly with the increase in etching time. Both ZEP-520-22 and SAL-602-SR2 gave the same results. The etch-stop problem was considered to be mass-balance between the condensed layer below the resist and the gas phase. When AHF etched SiO@sub 2@ film on Si substrate, notching profile was observed during the over-etching process.

PS-MoP30 Self-Aligned Contact Etch Development for 90nm Technology Node*, **M.G. Sedigh**, H. Lee, J. Zhang,* Cypress Semiconductor*; J. Stinnett, A. Joshi,* Applied Materials, Inc.

Self-aligned contacts play a significant role in driving down the cell size in CMOS-based memories, in particular DRAM and SRAM. We present development results of self-aligned contact etch for SRAM 90 nm technology node. Requiring high SiO@sub 2@, Si@sub 3@N@sub 4@, P.R. selectivity and vertical profile, combined with constrained imposed on the process by using 193 nm P.R. and organic BARC (required for improving lithography process window) and ever-present need for well-formed big structures in open area (i.e. overlay measurement marks) form the boundary of our development efforts. Summary of development effort starting from early stage (tool selection, chemistry selection, CIP etc.) and resolving specific failure modes (striation, CD bias, reverse microloading, etc.) will be presented. Some shortcomings and deficiencies with current tool/architecture followed by our recommendation for eliminating them toward next generation dielectric etch will be also discussed.

PS-MoP31 Atomic Layer Etching of Silicon using a Low Angle Forward Reflected Ar Neutral Beam*, **S.D Park**, D.H. Lee,* Sungkyunkwan University, South Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea

Atomic layer etching (ALE) is expected to be a very important process for the fabrication of future nano-scale devices, because current dry etching techniques could not strictly control the etch depth in nono-scale because of their high etch rates. In addition, relatively high energy of the ions can damage the crystal surface. Therefore, many studies on ALE of Si have been reported in recent years to develop a technique to etch materials layer-by-layer. But, these previous methods may show charging damage due to the charged particles such as positive ions and photons generated in the plasma. Therefore, in this study, ALE of Si was carried out using a sequential Cl2 adsorption and an Ar neutral beam irradiation instead of ion beam. Low energy Ar neutral beam was generated by a low-angle forward reflected neutral beam technique. ALE of Si is a cyclic process consisting of 4 steps: (1) adsorption of Cl2 on Si surface, (2) evacuation, (3) Ar neutral beam irradiation to the surface, (4) evacuation of etch products. The etch process parameters for optimizing the atomic layer etching of Si are Cl2 gas exposure time, Ar neutral beam irradiation time, Ar neutral beam energy, etc. It is expected that the etch rate per cycle increased with the chlorine supplying time and saturated to a constant value of about 1.36â"« per cycle which corresponds to the one mono-layer thickness of Si. The surface damage was estimated using transmission electron microscopy (TEM). The step height divided by the total number of ALE cycles yielded the etch rate per cycle. A scanning electron microscope (SEM) was used to observe as-etched Si profiles and an atomic force microscope (AFM) was used to analyze the surface topography.

PS-MoP32 Vertical Platinum Etch Profile for Electrode of High-K Dielectric Materials with Cl@sub 2@/Ar/C@sub 4@F@sub 8@ Plasma*, **C.W. Kim**, H.-Y. Song, Y.H. Choi, S.G. Yang,* Inha University, South Korea*; J.G. Lee,* Bucheon College, South Korea*; S.-G. Lee, B.-H. O, I.H. Lee,* Inha University, South Korea*; S.-G. Park,* Inha University, South Korea, Korea, Republic of

In this paper, we investigate the characteristics of the platinum dry etch using Cl@sub 2@/Ar/C@sub 4@F@sub 8@ gas with ICP(Inductively Coupled Plasma) source. Platinum is widely used as electrode of high-k dielectric materials and the vertical side wall slope of electrode is important especially in the fine pattern process for ultra large scale integration. The etch selectivity of platinum to photoresist is improved from 1:1 to 1.6:1 by C@sub 4@F@sub 8@ gas addition to Cl@sub 2@/Ar gas and this leads to very anisotropic Pt sidewall etch angle of 80° even with the photoresist masking. We studied the C@sub 4@F@sub 8@ addition effect by monitoring the variation of active plasma species with QMA(Quadruple Mass Analyzer) and analyzing the residue of etched surface.

PS-MoP33 Process Consideration in MRAM Metal Etch*, **S. Kanakasabapathy**,* IBM T.J. Watson Research Center

Magnetic Random Access Memory (MRAM) holds the promise to evolve into a non-volatile universal memory@footnote 1@,@footnote 2@. The MTJ stack comprises of a top data storing magnetic film that is separated by a thin Tunnel Barrier in the order of 10A from a bottom magnet@footnote 3@. MTJ patterning involves etching of non-volatile magnetic alloys without the benefit of a high thermal budget. The sidewall redepositon of the etch products is a key yield detractor in these etches@footnote 4@. Besides tapering the profile to achieve sidewall cleaning, stopping on the very thin tunnel barrier is considered an option to minimize this detractor. We present in this paper, such options and contrast them. @FootnoteText@ @footnote 1@W.J. Gallagher et al,"Microstructured Magnetic Tunnel Junctions", Journal of Applied Physics, 81, p.3741 (1997).@footnote 2@S. Tehrani et al,"High Density Submicron Magnetoresistive Random Access Memory", Journal of Applied Physics, 85, 5882 (1999).@footnote 3@S.S.P Parkin et al, "Exchange Biased Magnetic Tunnel Junctions and Application to Nonvolatile Random Access Memory", Journal of Applied Physics, 85, 5828 (1999).@footnote 4@R. Ditizio et al, "Cell Shape and Patterning Considerations for Magnetic Random Access Memory (MRAM) Fabrication", Semiconductor Manufacturing Magazine, January 2004. .

PS-MoP34 A Zero-order Semi-Empirical Physical Model for Chemically-Enhanced Physical Vapor Deposition (CEPVD) of Ta(C)N}*, N. Li,* ***D.N. Ruzic,***
University of Illinois at Urbana-Champaign

Chemically-enhanced physical vapor deposition (CEPVD) is a new technique having the potentiality to deposit films with physical vapor deposition (PVD) quality and chemical vapor deposition (CVD) step coverage. A Ta target is sputtered in a magnetron system with the metal-organic precursor vapor, TBTDET, in combination with a reactive (N2) gas and a secondary RF plasma. CEPVD film properties have demonstrated wide range of variation with the processing parameters. For instance, by controlling the processing the film resistivity drops dramatically from nearly insulating to about 250 ï•-ï•-ï?-cm. Therefore a zero-order semi-empirical model is established correlating the processing parameters with the target and film surface coverage by Ta, TaN and organic sites, which predicts the target operation mode, and the film elemental composition. The physical component of the model involves the calculation of the plasma properties, reactive sputtering, transportation and deposition of the three kinds of surface sites. The chemical reactions are represented as elementary gas phase reactions enhanced by electron impact, H reducing and ion bombardment. The rate constants are derived by simulation curve fitting with the AES experimental data. The organic by-products accounting for the detection of carbon on the substrate by AES analysis and poisoning of the target are categorized into non-volatile product (OR1) and volatile product (OR2) in a lump-sum assumption. Simulation results are compared with the experiment data with different RF power, bias voltage, pressure, carrier gas flow rate, TBTDET vapor pressure etc, and the deviation is consistently below 25 %. For example, the simulation shows that at certain working conditions the carbon concentration decreases from 61% to 54% as the substrate voltage changes from 0V to -60V, which corresponds to the AES result that the carbon concentration decreases from 51% to 43%.

Electronic Materials and Processing
Room 304C - Session DI+PS-TuM

High-k Dielectrics: Growth and Processing

Moderator: A.A. Demkov, Motorola, Inc.

8:20am **DI+PS-TuM1 Inductively Coupled Remote Nitrogen Plasma Treatment of Hf Based Gate Dielectrics for Improved Interface Stability on Si(100)**, ***T. Klein,*** University of Alabama **INVITED**

HfO@sub 2@ is a leading candidate for replacement of SiO@sub 2@ in CMOS field effect transistors. Past work has shown this material has a tendency to interdiffuse and react with the substrate forming a less-than-ideal abrupt interface. In this paper, HfO@sub 2@ thin film stability results for a remote plasma nitrification process is reported in which the Si substrate is exposed to a N@sub 2@/He plasma then annealed in vacuum before the gate oxide deposition process. The nitrided surface and subsequently deposited films were studied using ellipsometry and x-ray photoelectron spectroscopy before and after annealing treatments. This method is compared to other procedures for the addition of nitrogen developed in our laboratory including the plasma enhanced deposition of HfO@sub 2@ using N@sub 2@O and N@sub 2@ plasmas, and post deposition treatment of the films with a remote N@sub 2@ plasma. Nitrogen plasma treated substrates showed a nitride layer approximately 16 @Ao@ thick which was sufficient to prevent significant film/substrate interdiffusion and thickness growth for 2 min., 800@degree@C anneals in Ar.

9:00am **DI+PS-TuM3 In Situ Infrared Spectroscopy of High-k Dielectric Growth on Si (100)**, ***R.T. Brewer,*** *M.-T. Ho, L. Ghoncharova,* Rutgers University*; M.P. Boleslawski,* Aldrich Chemical Co.*; T. Gustafsson, E. Garfunkel, Y.J. Chabal,* Rutgers University

We have used in situ, transmission infrared (IR) spectroscopy and ex-situ Medium Energy Ion Scattering (MEIS) to investigate the growth mechanisms of atomic layer deposition (ALD) of Al@sub 2@O@sub 3@ and HfO@sub 2@ on Si (100). The high-k materials were deposited by alternating exposures of organometallic precursors (trimethylaluminum for Al@sub 2@O@sub 3@ and tetrakis(ethylmethylamido)hafnium for HfO@sub 2@) and D@sub 2@O at ~300@super o@C. IR spectroscopy makes it possible to identify the adsorbed precursor products, the growth of the high-k films, and the formation of an interfacial layer, such as SiO@sub 2@. For ALD directly on hydrogen terminated Si (100) we observe the formation of interfacial SiO@sub 2@; moreover, several ALD exposure cycles are required before the high-k film can nucleate on the surface and begin to grow. Functionalizing the surface with a pretreatment of NH@sub 3@ results in high-k film growth from the first cycle exposure, and reduces the formation of interfacial SiO@sub 2@ by acting as a barrier and providing a nucleation layer for the high-k growth. In this talk, we will compare HfO@sub 2@ and Al@sub 2@O@sub 3@ growth.

9:20am **DI+PS-TuM4 DFT Study of the Initial ALD Reactions of Hf(N(CH3)2)4 on the SiO2 and Si-H Surfaces: Mechanism, Kinetics, Vibrational Spectra and Interface Structure**, *J.G. Han,* ***C.B. Musgrave,*** Stanford University*; M.J. Kelley, G.N. Parsons,* North Carolina State University

Atomic layer deposition is ideally capable of depositing uniform thin films of materials one atomic layer at a time. In practice, the initial coverage of active sites on the starting substrate determines the initial growth rate, which is typically below the steady state growth rate. Furthermore, the initial reactions on the starting substrate are important in defining the atomic structure of the interface between the deposited film and the substrate. Because the electronic properties of advanced CMOS are highly sensitive to the electronic structure and thus the atomic structure of this interface, it is essential to gain control over the structure of the interface through the chemistry of the ALD process on the starting substrate. We have used ab initio electronic structure theory to calculate mechanisms leading to various interface structures for the reaction of a tetrakis(dimethylamido) hafnium precursor with Si-H and Si-OH terminated substrates and the resulting interface bonding. We also calculate the vibrational spectra for some possible surface species and compare these with those measured by FTIR. Our calculations show that the adsorbed metal precursor activates neighboring Si-H sites enabling subsequent reactions with water and the ALD metal precursor.

9:40am **DI+PS-TuM5 Development of Post Etching Process for Hf Based High-K Gate Dielectric**, ***W.S. Hwang***, *J.H. Chen, W.J. Yoo, D.S.H. Chan,* National University of Singapore, Singapore*; D.-L. Kwong,* University of Texas at Austin

For successful integration of high-K dielectrics into CMOS process, a technique to selectively remove high-K films and interfacial layers with minimum consumption of both Si substrate and shallow trench isolation SiO@sub 2@ needs to be developed. In this work, we studied the wet etching properties of Hf based high-K dielectrics using 1% HF (DHF) for HfO@sub 2@, HfSiO, and HfAlO deposited by atomic layer deposition or sputtering. Effects of anneal, plasma oxidation and nitridation are discussed. Results show that before anneal, all these films can be removed completely by DHF with etch rates higher than 12nm/min. After 700@super o@C anneal, etch rate of HfAlO does not change, whereas etch rate of HfSiO decreases ~ 50%, leaving ~ 1nm thick densified HfSiO interfacial layer unremoved. Furthermore, HfO@sub 2@ cannot be etched by DHF after anneal: after etching for 24 hours, no thickness change was observed. By applying the room temperature plasma oxidation treatment, HfSiO interfacial layer can be removed in 10s in DHF, but 3-6nm thick SiO@sub 2@ grows underneath HfSiO interfacial layer, resulting in significant recess into Si substrate. However, 2 nm thick HfO@sub 2@ can be removed in 10s in DHF without noticeable recess into Si substrate, by applying the room temperature plasma nitridation treatment. Surface analysis using X-ray photoelectron spectroscopy shows that Hf-N bonds are formed on the surface of HfO@sub 2@ after plasma nitridation. High etch rate of HfN of 1000Å/min in DHF can explain the increase of the etch rate by the incorporation of N. HfSiO interfacial layer was also removed in 10s after plasma nitridation. By the plasma nitridation aided DHF cleaning process, very little recess of both Si substrate and STI SiO@sub 2@ was achieved, and furthermore low contact NiSi sheet resistance of 4-5@ohm@/sq was achieved.

10:00am **DI+PS-TuM6 Plasma-Enhanced Atomic Layer Deposition for Compositionally Controlled Metal Oxide Thin Films**, ***S.X. Lao***, *R.M. Martin, 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 and higher processing yield. In this work, ZrO@sub 2@ and HfO@sub 2@ films were deposited using zirconium and hafnium tetra-tert butoxides as the metal precursors and oxygen radicals generated from oxygen plasma as the oxidant, introduced in alternating, cyclical sequence. 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. Optical emission spectroscopy (OES) was utilized to identify and quantify the gas phase atomic radicals. It was found that the OES intensity of oxygen radicals varies inversely with that of hydrogen radicals originating from the precursor. The presence of oxygen and hydrogen radicals in the gas phase resulted in the formation of surface hydroxyl groups, an important surface functional group for the chemisorption of precursors. As measured by the Fourier transform infrared spectroscopy (FTIR), the -OH integrated absorption intensities increased linearly with the number of deposition cycles and decreased upon annealing. Atomic force microscopy (AFM) analysis showed fairly smooth films with an RMS roughness of 1.7 Å after 5 deposition cycles. MOS capacitors were fabricated with the PEALD deposited films. The capacitance-voltage (C-V) and current-voltage (I-V) measurements showed that the PEALD HfO@sub 2@ films had the highest dielectric constant of 25 with an equivalent oxide thickness (EOT) of 12.5-15 Å. The leakage currents were several orders of magnitude less than that of SiO@sub 2@ films at the same EOT.

10:20am **DI+PS-TuM7 DFT Investigation of Initial HfO@sub 2@ Atomic Layer Deposition on Nitrided Silicon Surface**, ***Y. Xu,*** *C.B. Musgrave,* Stanford University

The atomistic mechanism of the initial atomic layer deposition (ALD) reactions of hafnium oxide on a nitrided silicon surface was investigated using density functional theory (DFT). Reactions involving two different metal precursors are explored: Tetrakis-dimethylamido-hafnium (Hf[N(CH@sub 3@)@sub 2@]@sub 4@) and hafnium tetra chloride (HfCl@sub 4@). Hf[N(CH@sub 3@)@sub 2@]@sub 4@ forms no adsorbed complex on the nitrided Si substrate. The ALD ligand exchange reaction requires a barrier of 0.63eV and is exothermic by 0.22 eV. The adsorbed

precursor state is not formed because the Hf atom of the precursor state has full s and d-shells and the amines are doubly bonded to Hf. Furthermore, the lone pair of nitrogen on the nitrided silicon surface is somewhat delocalized, reducing its ability to form dative bonds. Reaction between HfCl@sub 4@ and the nitrided silicon surface results in adsorbed HfCl@sub 4@ complex with an adsorption energy of 0.66 eV. The ligand exchange barrier is 1.33eV relative to the complex structure and the overall reaction is endothermic by 0.50 eV. Consequently, the alkylamide precursor is both kinetically and thermodynamically superior to HfCl@sub 4@ for the initial ALD reactions on the nitrided surface. We previously showed that for ALD of HfO@sub 2@, Hf[N(CH@sub 3@)@sub 2@]@sub 4@ appears to be a better choice than HfCl@sub 4@ both thermodynamically and kinetically. Thus Hf[N(CH@sub 3@)@sub 2@]@sub 4@ precursor performs better for both the initial reaction on the nitrided silicon surface and subsequent ALD of the HfO@sub 2@.

10:40am **DI+PS-TuM8 Oxygen Transport Properties in Hafnium Silicate Films***, D. Starodub,* ***L. Goncharova****, E. Garfunkel, T. Gustafsson,* Rutgers University*; G. Bersuker, B. Foran, P. Lysaght,* International Sematech

Developing an understanding of the kinetics and thermodynamics of film growth during fabrication of CMOS high-K gate stacks is thought to be critical in enabling control of interfacial layers, defects and other film properties. In this presentation we present new results on the oxygen transport mechanisms and kinetics in hafnium silicate films as a function of composition, structure and annealing conditions. The silicate films were grown on Si(001) substrates with and without nitride incorporation. To study oxygen transport, incorporation and interfacial growth, reoxidation of as grown and annealed films was performed in isotopically labeled oxygen-18. Oxygen isotopic distributions were then measured using high-resolution medium energy ion scattering. With a nitride layer present, the interface oxidation was minimized, and reaction with oxygen was limited to exchange with network oxygen in the silicate film. This exchange saturated with time and appeared to be enhanced after film recrystallization, perhaps due to an increase in grain boundaries. The films directly grown on H-terminated substrates exhibited additional oxygen incorporation at the interface with SiO@sub 2@ formation. This process increases with increasing film crystallinity, opening more permeable diffusive pathways via crystallite grain boundaries. We also explore PDA effects on oxygen permeability of the silicate films.

11:00am **DI+PS-TuM9 Investigation of the Roles of Oxygen Plasma and Solvent in the Pulsed-Liquid Injection PE-MOCVD Deposition of Y@sub2@O@sub3@ High-@kappa@ Materials in MIM Structures***,* ***C. Vallee****, C. Durand, M. Derivaz, M. Kahn, M. Bonvalot,* CNRS, France

CMOS scaling and Metal-insulator-Metal (MIM) capacitance density improvement will require use of new high-@kappa@ dielectric material in a near future. We have focused our work on the elaboration of Y2O3 thin films at low thermal budget (350°C) by pulsed-liquid injection Plasma Enhanced MOCVD for MIM capacitors (TiN-Y2O3-TiN). In this technique, dissolved Yttrium @beta@-diketonate Y(tmhd)@sub 3@ precursors (in cyclohexane and octane) are sequentially injected into an evaporator, with accurate reproducibility in the amount of precursors delivered to a low frequency (380 KHz) plasma chamber, where a O@sub 2@ plasma is applied to induce precursor decomposition and surface reactivity. The respective roles of oxygen plasma and solvent composition in the Y2O3 high-@kappa@ materials characteristics and interface properties have been investigated. The plasma is monitored by optical emission spectroscopy (OES) while films and interfaces are mainly characterized by X-rays Photoelectron Spectroscopy (XPS). Electrical characterizations are also performed in order to obtain capacitance density, voltage linearity and electrical breakdown properties. We have shown that a low plasma power and a high pressure limit carbon contamination while a high injection frequency limits interface reactions (as observed on SiO2/Si substrates). With this technique a capacitance density up to 6 fF/µm@super 2@ has been obtained. We have also investigated the effects of two solvents, cyclohexane and octane, in this study : it has been observed that deposition rate is strongly influenced by solvent nature. In addition, we also studied the effect of nitrogen plasma before, during and after deposition. Chemical bonding, concentration, and distribution of N in Y-oxide films after deposition and after high-temperature annealings are also characterized. The N concentration distribution in high-k dielectrics is likely to be an important factor to achieve optimal electrical performances.

11:20am **DI+PS-TuM10 UV Activated Surface Preparation of Silicon for High-k Dielectric Deposition***,* ***C.C. Finstad****, A.J. Muscat,* University of Arizona

High-k gate materials, such as HfO@sub 2@, are unstable on silicon, readily forming a low permittivity interfacial oxide when heated. A single layer of silicon nitride grown prior to gate dielectric deposition could serve as a diffusion barrier to prevent oxide formation. Moreover the SiN layer should promote nucleation of the dielectric film, thereby acting as both a barrier and a seed layer. A monolayer film of surface amine groups will be chemically similar to the hydrogen atoms of surface hydroxyl groups; therefore a pin-hole free monolayer of amine groups should simultaneously serve as both a diffusion barrier and a seed layer. This study aims to deposit a thin, continuous layer of surface amines at low temperatures (5.8 eV can photodissociate NH@sub 3@ molecules to yield NH@sub 2@ photofragments that react with H-terminated Si surfaces. With UV activation, N coverage increased with time and saturated at 1.7 ML. @FootnoteText@ @footnote 1@A. Nakajima et al., Appl. Phys. Lett. 80 (7), 1252 (2002).

11:40am **DI+PS-TuM11 Annealing of Hafnium Oxide Grown on Silicon by Atomic Layer Deposition: Changes in Interfacial Structure***, A. Deshpande,* University of Illinois at Chicago*; R. Inman,* ***G. Jursich,*** American Air Liquide*; C. Takoudis,* University of Illinois at Chicago

Thin films of hafnium oxide are deposited on Si(100) substrates by means of atomic layer deposition (ALD) using tetrakis(diethylamino)hafnium as the hafnium precursor and subsequently annealed at various temperatures (600-1000 C) under Ar atmosphere. The resulting composition and purity of the films are determined at different substrate temperatures using x-ray photoelectron and Fourier transform infrared (FTIR) spectroscopies. The chemical and physical structure of the film/interfacial regions are analyzed using a combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope. Depth profiling of film/interfacial regions were obtained using high-resolution angle resolved x-ray photoelectron spectroscopy (XPS). The pre-annealed films showed presence of a very thin silicon oxide at the film/substrate interface that originated from the residual surface oxide resulting from the wet chemical surface cleaning procedure used. Thus, no growth of interfacial region is observed from deposition alone. However, the post annealed films show increase in interfacial silicon oxide thickness coupled with formation of silicate-like structure as the annealing temperature is increased. This is evident from independent sets of data of FTIR spectroscopy and XPS. At the highest annealing temperature used (i.e., 1000 ÂºC), formation of silicide is observed at the interface. From these measurements detail information on the interfacial changes incurring from thermal annealing are obtained when there is a very thin layer of silicon oxide present on the silicon substrate. These results will be discussed in view of the intermediate SiO2 in terms of HfO2:SiO2 inter-diffusion and the formation of silicate-like structure.

Plasma Science and Technology
Room 213A - Session PS1-TuM

Dielectric Etching

Moderator: E.A. Hudson, Lam Research Corp.

8:20am **PS1-TuM1 Polymer Formation in Fluorocarbon Etch Plasmas***,* ***B. Ji,*** *S. Dheandhanoo, S.A. Motika, P.R. Badowski, J.R. Stets, E.J. Karwacki,* Air Products and Chemicals, Inc.

Recent investigations have shown fluorocarbon (FC) polymers play several key roles in dielectric etch plasmas. A steady state FC film is a key ingredient for etching silicon under ion bombardment. For anisotropic dielectric etching, FC films protect the photoresist mask and passivate the feature sidewalls. In recent years, the semiconductor industry have adopted heavier molecular weight and lower fluorine to carbon ratio gases, such as c-C@sub 4@F@sub 8@, C@sub 5@F@sub 8@, and C@sub 4@F@sub 6@ for anisotropic dielectric etching. In this study, we investigate the correlation between fluorocarbon molecular structure and FC film property. We employ mass spectrometry to determine electron impact fragmentation patterns of various fluorocarbon molecules. We use Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy to characterize the FC polymer structure. We investigate a series of novel dielectric etch gases such as c-C@sub 4@F@sub 8@, C@sub 4@F@sub 8@O, C@sub 3@F@sub 6@, C@sub 3@F@sub 6@O, C@sub 5@F@sub 8@, C@sub 4@F@sub 6@, and C@sub 6@F@sub 6@ etc. The results demonstrate that FC film properties depend not only on the atomic

fluorine to carbon ratios, but also on the bonding structures in the molecules. Finally, we correlate the molecular fragmentation patterns and FC film properties to anisotropic dielectric etch performances of various gases.

8:40am **PS1-TuM2 Reduction of Line Edge Roughness for 90nm Technology Node for Contact and Trench Etched Features***, **D. Farber**,* Texas Instruments, Dallas*; W. Dostalik, B. Goodlin, R. Kraft, T. Lii,* Texas Instruments

For the 90nm technology node, methods for reducing line edge roughness (LER) during dielectric etch are shown. Two particular, distinct cases are demonstrated here: 1) contact holes etched in phosphorus-doped glass (PSG), and 2) trench lines in organo-silicate glass (OSG) low-K dielectric for damascene Cu interconnect. For both cases, an etch strategy is developed to deal with the inherent roughness and granularity of 193nm photoresist while maintaining adequate CD control and resist thickness margin. Using an image processing technique, an effort is made to quantify the degree of LER associated with the processes.

9:00am **PS1-TuM3 Effect of Non-sinusoidal Bias Voltage Waveforms on Ion Energy Distributions and SiO@sub 2@/Si Etch Selectivity in Fluorocarbon Plasmas@footnote 1@***, **A. Agarwal**, M.J. Kushner,* University of Illinois at Urbana-Champaign

During plasma etching, ion energy distributions are typically coarsely controlled by varying the amplitude of a rf sinusoidal bias voltage and/or controlling the dc bias. The resulting ion energy distribution (IED) is often broad compared to the differences between threshold energies of surface processes. Controlling the width of the IED can potentially help maintain critical dimensions of features and improve selectivity. In high-plasma density, low gas pressure systems, sheaths are typically collisionless and so additional control over IEDs can be obtained by controlling the sheath voltage. In this regard, non-sinusoidal bias waveforms have been proposed as a means to tailor the IEDs.@footnote 2@,@footnote 3@ In this talk, we report on results from a computational investigation of IED control by using a tailored non-sinusoidal bias voltage waveform. A 2-dimensional plasma equipment model has been linked with a Monte Carlo feature profile model to assess the consequences of the resulting IEDs on the selectivity of etching SiO@sub 2@ to Si in fluorocarbon ICP plasmas and capacitively coupled plasmas. The most stringent control over the IEDs is obtained at lower frequencies where sheath crossing times are short compared to the rf period and in gas mixtures where the masses of the ions are similar. Slightly more collisional plasmas (provided the sheath remains collisionless) also provide more stringent control by reducing the energy of ions entering the sheath proper. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF. @footnote 2@ S. B. Wang and A. E. Wendt, J. Vac. Sci. Technol. A, 19, 2425 (2001) @footnote 3@ S. Rauf, J. Appl. Phys., 87, 7647 (2000).

9:20am **PS1-TuM4 Dielectric Processes Enhancements Using Multifrequency Sheath Modulation***, **S.C. Shannon**, A.M. Paterson, T. Panagopoulos, D. Hoffman, J.P. Holland,* Applied Materials, Inc.*; D. Grimard,* University of Michigan

Dual frequency capacitive discharges have become the new standard in dielectric etch processing. Typically, frequencies are selected such that bulk plasma dissociation and plasma sheath dynamics can be independently controlled. Recently, dual frequency development has focused on the interaction of the two frequencies in the sheath surrounding the plasma. In this paper, a model is presented where a symetric discharge is driven by an RF current with multiple frequency components. The impact of these multifrequency sheath dynamics on ion energy distribution and the process tunability in dielectric etch processes using this technology is presented.

9:40am **PS1-TuM5 A Novel Etching Process Employing Pulse-Modulated Electron-Beam-Excited Plasma for Fabrication of Micro-Optical Devices***, **K. Takeda**,* Nagoya University, Japan*; Y. Tomekawa, T. Ohta,* Wakayama University, Japan*; K. Yamakawa,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan*; M. Hori,* Nagoya University, Japan

Recently, micromachining of optical devices such as core lens on the edge of optical fiber attracts much attention. In this process, the fast atomic-beam etching (FABE) or the ion-beam etching (IBE) has been employed, since the conventional reactive plasma etching cannot be employed as the radio-frequency self-biasing is not efficiently supplied to the thick dielectric materials. However, the etch rates of FABE and IBE are typically around a few tens nm/min, which are very low compared with the reactive ion etching. Therefore, novel processes to realize the higher etch rate are strongly required to reduce the processing time. We have proposed a SiO@sub2@ etching employing an electron-beam-excited plasma (EBEP) for the fabrication of micro-optical devices. The dc-EBEP have realized the high etch rate without any additional bias power supply. However, it had problems such as the thermal damage of the photo resist, non etch-uniformity and instability of plasmas. In this study, we have developed a novel etching process for the fabrication of micro-optical devices employing a pulse-modulated EBEP and have investigated the etching characteristics. Plasma was generated at a total pressure of 0.27Pa and the fed gases were C@sub4@F@sub8@/Ar, a discharge current of 25A and an electron beam acceleration-voltage (V@subA@) of 100V with a pulse-modulation frequency of 50kHz and 50% duty ratio. The pulse-modulated EBEP have been found to have a great potential to realize the high etch rate of 375nm/min with 0.75mm hole-pattern and improve some problems in the dc-EBEP. Moreover, from the results of the optical emission spectroscopy, F atom density was reduced with the decrease of the duty ratio of V@subA@. Therefore, We performed the anisotropic SiO@sub2@ etching with a high rate by the ion assisted etching without any self-biasing power supply. Consequently, the micro-fabrication of core lens on the edge of optical fiber was successfully carried out.

10:00am **PS1-TuM6 Surface Kinetics Modeling for Silicon Oxide and OSG Etching in Fluorocarbon Plasmas***, **O. Kwon**, B. Bai, H.H. Sawin,* Massachusetts Institute of Technology

Fluorocarbon plasma for silicon oxide or OSG etching is a complicated system involving many ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity to photoresist. For a better understanding of the process it is necessary to have an appropriate surface kinetics model which includes simultaneous etching and deposition. We have developed a novel surface kinetics modeling approach, Translating Mixed Layer (TML) model that is based on the assumption that the surface layer is a well-mixed region due to energetic ion bombardments. The mixed layer thickness is given the depth associated with ion bombardment, i.e. ~2.5 nm. The etching and deposition reactions are modeled based on the elemental composition of this layer using a lumped kinetic model. The lumped kinetic model was constructed and verified using measured oxide etching yield data determined by quartz crystal microbalance (QCM) in conjunction with plasma neutral and ion concentrations/fluxes determined by mass spectrometry of C2F6 and C4F8 discharges over broad ranges of process conditions. Etching chemistries with low atomic fluorine concentration (e.g. C4F8 chemistry) exhibit etching yields that are sensitive to compositional change in the plasma. In chemistries with high atomic fluorine concentration (e.g. C2F6 chemistry); however, the etching yield is less sensitive to compositional change in the plasma. Based on the measurements and the simulation, a lumped oxide etching surface kinetics model was constructed. In this model, adsorbed fluorocarbon species act as the etchant and the etching yield is determined by the composition of the surface layer. Atomic fluorine acts as a fluorocarbon etchant to control the etching yield. The model was also applied to OSG etching with fluorocarbon chemistry. The model successfully predicts the etching characteristics of OSG film.

10:20am **PS1-TuM7 Study on Self-aligned Contact Oxide Etching Using C@sub 5@F@sub 8@/O@sub 2@/Ar and C@sub 5@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ Plasma***, **S.B. Kim**, D.G. Choi, D.S. Kim, Y.W. Song,* Hynix Semiconductor Inc., Korea*; C.I. Kim,* Chung-ang University, Korea

A self-aligned contact (SAC) technology is developed for application of electrical contacts between the local interconnection and the silicon diffusion regions (or plug pad) from 0.18µm device. The commercial memory devices have capping (or spacers) nitride (Si@sub 3@N@sub 4@) for protection of Word Line (or Bit Line) and nitride thin film layer for etching stop of SAC. Recently, the problems of SAC etch process in ULSI devices of sub 0.1µm-design rule are low selectivity to nitride and etching-stop due to high aspect ratio of contact hole. The key issue of SAC etch process is control of polymer generation. In this study, the characterizations of SAC oxide etching are investigated with C@sub 5@F@sub 8@/O@sub 2@/Ar and C@sub 5@F@sub 8@/O@sub 2@/Ar/CH@sub 2@F@sub 2@ plasma. As the mixing ratio of O@sub 2@ on the C@sub 5@F@sub 8@/Ar/O@sub 2@ increase, the amount of polymer decreases and the ability of contact etching increases, the effect CH@sub 2@F@sub 2@ addition on SAC oxide (SiO@sub 2@) etching in C@sub 5@F@sub 8@/Ar/O@sub 2@ is that etch rate of oxide in the contact hole increases about 7%, and the selectivity of oxide to nitride increase, specially that to nitride of contact bottom for SAC etch stopping increases. The selectivity of oxide to nitride increases with increasing of

plasma source power or with decreasing of bias power. SAC patterned wafers were characterized using top-down critical dimension scanning electron microscopy (CD-SEM), cross-section SEM, and transmission electron microscopy (TEM). To analyze the effect of various parameters on the C@sub 5@F@sub 8@/Ar plasmas, we investigated the chemical species in the gas phase with an optical emission spectroscopy (OES). The components of polymer were investigated with transition electron microscopy - energy dispersive X-ray (TEM-EDX) and auger electron spectroscopy (AES). X-ray photoelectron spectroscopy (XPS) studies have analysis of real polymer topology on contact bottom and side wall.

10:40am **PS1-TuM8 Advanced Inductive Plasma Etcher for Low-k Materials and Oxide**, ***G. Vinogradov***, *A. Kelly, V.M. Managarishvilil, Y. Hirano,* FOI Corporation, Japan

A new kind of ICP dielectric etcher has been tested on a variety of materials and patterns and showed produciton worthy results. There is presently only one type of commercial 300-mm equipment for advanced SiO@sub 2@ dry etch: narrow-gap capacitive. Flat inductive plasma sources do not provide radial uniformity in narrow gap designs. An increase of the discharge gap (volume) improves uniformity but substantially increases gas residence time thus decreasing selectivity to photoresist. Another problem is instability of known flat ICP etchers due to capacitive sputtering of the dielectic plate separating ICP coils from plasma volumes. Flat inductive sources, therefore, were not yet successful for advanced oxide etch. A novel inductive narrow-gap 300-mm GroovyICP@super TM@ plasma etcher having substantially flat geometry for advanced etch of low-k materials (organic and inorganic) and oxide in one multiprocess chamber was developed and tested in production. It incorporates three mutually embedded geometrically separate and independently adjustable ring-shape inductive plasma sources designed as annular grooves in a flat roof made of silicon or ceramics. Every coil/plasma ring has independent RF power supply thus achieving controllability over the radial power distribution. Process results obtained with our 300-mm etchers will be presented in order to show principal features and exclusive controllability of the new plasma source and manufacturing tools.

11:20am **PS1-TuM10 Impact of Vibrational States on Dissociation in Fluorocarbon and Hydrogenated Fluorocarbon Plasmas**, *S. Adamson, K. Novoselov, A. Dement'ev, V. Kudrja,* Soft-Tec, Russia; *S. Rauf,* ***P.L.G. Ventzek***, Freescale Semiconductor

Vibrational states of polyatomic molecules are known to have an important effect on the energy balance in plasmas and as such the plasma chemical kinetics. Less often considered is the impact of the population of vibrational states on individual processes associated with one species in which multiple vibrational states are often lumped. High density plasmas used for plasma processing may be characterized by relatively large gas temperatures (>700K) allowing for population of some low lying energy vibrational states. The presence of an ensemble of a few low lying energy states is significant as the cross-sections defining the transition to dissociation from states above ground may be quite different than those from ground. The dissociation processes associated with C4F6 and other CxHyFz plasmas are explored by treating the dissociation processes as bi-molecular using a diatomic model with the energies of the vibrational states being the states of the mode associated with the two pre-linked dissociating units. While not fundamental modes, they provide a means of exploring the scaling of electron impact reaction rates with temperature. Further they facilitate the exploration of assumptions built into simulations used to extract transport parameters for plasma process simulation (e.g., electron swarm simulations). In this presentation, the scaling of electron transport parameters and reaction rates for various electron impact processes with gas temperature and gas mixture are parameterized. These results are complemented with illustrative integrated equipment and feature scale simulations.

11:40am **PS1-TuM11 Measuring Macro- and Micro-loading Impact on Etch Bias**, ***H.P. Stadniychuk***, Cypress Semiconductor

Ever smaller critical dimensions (CD) and tighter budgets call for minimization of device-to-device differences in the fab. While all devices typically share the same design rule for the targeted feature on any given layer, pattern density variation became a significant contribution to the observed CD variation. In this study pattern density effect on STI (Shallow Trench Isolation) - type etch was characterized on local (hundreds of microns) and global (wafer) scales while keeping pitch the same and ARDE (Aspect Ratio Dependent Etch)-effects constant. One the challenges were to determine what constitutes the local scale and how data can be collected without using special masks. It was found that etch bias is twice more sensitive to variation in local pattern density than to the global. Methodology for proper accounting pattern density-induced CD variation in process development as well as strategies for compensating these effects will be discussed.

Plasma Science and Technology
Room 213B - Session PS2-TuM
New Gate Conductor Etching

Moderator: C. Labelle, Advanced Micro Devices

8:20am **PS2-TuM1 Study of Refractory Metal Nitrides/HfO@sub 2@ Gate Stack Etching Using Inductively Coupled Plasma**, *J.H. Chen, W.S. Hwang,* ***W.J. Yoo***, *S.H.D. Chan,* National University of Singapore, Singapore; *D.-L. Kwong,* University of Texas, Austin

Metal gates/high-K gate stacks are expected to be used for 45nm and beyond MOSFETs, replacing conventional Poly-Si/SiON gate stacks. Refractory metal nitrides (RMNs) including TaN, TiN, and HfN are being studied extensively as the promising candidates for future metal gates, because of good thermal stabilities, and suitable work functions on hafnium based high-K dielectric for CMOS devices. In this work, we investigated the etching properties of RMNs (TaN, TiN and HfN) on HfO@sub 2@ using inductive coupled plasma (ICP) of HBr/Cl@sub 2@/O@sub 2@. Results show that the etch rate of ~2800Å/min for TaN, ~2500Å/min for TiN and ~4000Å/min for HfN can be achieved at 10mTorr in HBr/Cl@sub 2@ plasma (inductive power of 400W and DC bias of 144V). Etch rates of RMNs increase rapidly with increasing ion density and energy. The dependences of etch rates of TaN, TiN and HfN on ICP parameters are different, but all are more sensitive than that of poly-Si. Etch electivity of RMNs with respect to HfO@sub 2@ was lower, comparing to poly-Si/SiO@sub 2@ gate stack structure. Adding small amount of O@sub 2@ into Cl@sub 2@ or HBr plasma enhanced the etch selectivity of RMNs with respect to HfO@sub 2@, because it can suppress the etch rate of HfO@sub 2@, without a significant change the etch rates of RMNs. Improvement of etch selectivity can be also achieved by reducing ion energy and increasing pressure. Very anisotropic profile of these three RMNs metal gates can be acquired by reducing pressure, increasing ion energy and adding more Cl@sub 2@ in the gas mixture. Optical emissions at 400-800nm wavelength were observed from RMNs etch byproducts in Cl@sub 2@ or HBr plasma, providing sharp etch end point signal. X-ray photoelectron spectroscopy analysis of etched surfaces shows that most of etch byproducts of these three RMNs etched by Cl@sub 2@ or HBr plasma are volatile at 10mTorr and 100°C, and residues are found to be mainly bromides and chlorides.

8:40am **PS2-TuM2 Line Width Roughness Reduction for Advanced Metal Gate Etch and STI Etch with 193nm Lithography in a Silicon Decoupled Plasma Source Etcher (DPSII)**, ***T. Chowdhury***, *H. Lee, A. Renaldo, K. Ikeuchi, A. Habbermas, B. Bruggermann,* Cypress Semiconductor; *Y. Du, M. Shen, S. Deshmukh, J. Choi,* Applied Materials, Inc.

193nm lithography has become necessary as the critical dimensions of semiconductor devices continue to scale down towards sub 90 nm dimension. From a device point of view the effects of higher Line Edge Roughness (LER)/Line Width Roughness (LWR) are studied. Metrology aspects of LER/LWR are also included in the study. From dry etching perspective, however, 193nm resist brings new challenges due to its poorer plasma etch resistance, LER/LWR and lower thickness compared to 248nm DUV resist. This paper presents a successful development of advanced 0.1µm metal gate and STI etch application using 193nm lithography on Applied Materials' decoupled plasma etcher DPSII system. Process chemistry and process parameters for nitride mask step were thoroughly explored and investigated vs LWR. Post-etch measurement of line width roughness shows an average of 6nm LWR. It was observed LWR is a strong function of etch chemistry (CHF3/CF4 based HM open vs CH2F2 based HM Open), reaction regime (15 mT vs 30 mT) and ICP vs MERIE etc. A detailed study showing methods to reduce LWR is presented in this paper. .

9:00am **PS2-TuM3 Plasma Etching of Metal/High-K Gate Stack**, ***A. Le Gouil***, STMicroelectronics, France; *T. Chevolleau, G. Cunge, L. Vallier, O. Joubert,* LTM-CNRS, France; *P. Mangiagalli, T. Lill,* Applied Materials

The rapid downscaling of metal-oxide-semiconductor transistors imposes new materials for the gate stack. Metal gate electrode receives more attention than conventional poly-Si gate electrode when high permittivity material is used as the gate dielectric. In addition to the introduction of these new materials, critical dimension control of less than 3nm must be achieved for the 45 nm technological node. In this work the metal gate

etching process is developed with a poly-Si/TiN stack for the gate electrode and HfO@sub2@ (3.5 nm thick) as the gate dielectric. Anisotropic and selective etching of the gate stack requires the development of a multi-step etching process. First, the silicon part of the gate is etched using an HBr/Cl@sub2@/HeO@sub2@-based chemistry. We have then studied several chemistries (Cl@sub2@ , HBr and their mixture) to etch the TiN layer anisotropically and selectively with respect to HfO@sub2@. The selectivity and surface modification of the HfO@sub2@ layer after exposition to the plasmas have been studied by X-ray Photoelectron Spectroscopy and AFM. While highly anisotropic etching can be observed in pure Cl@sub2@ plasmas, a very rough HfO@sub2@ surface is observed in this case, partially due to the presence of TiO@subx@ residues on the HfO@sub2@ surface. In addition the selectivity toward HfO@sub2@ is poor. By contrast HBr provides a higher selectivity with less roughness. Hence using a mixture of HBr/Cl@sub2@ appears to be the best strategy to achieve both anisotropic and selective etching of TiN film over HfO@sub2@. Finally, a complete metal gate process requires HfO@sub2@ removal after the gate definition. We will show that this high temperature plasma process can seriously damage the gate profile due to the lack of passivation layer on the TiN sidewalls (undercutting is observed). This suggests that a protection layer must be formed after or during TiN etching in order to protect the metal gate before removal of the dielectric of the gate.

9:20am **PS2-TuM4 Etching Ruthenium with O2- and Cl2-Containing Inductively Coupled Plasma***, **C.-C. Hsu**, D.B. Graves, J.W. Coburn,* University of California, Berkeley

Ruthenium (Ru) plasma etching has been studied using inductively coupled plasma (ICP) with O2- and Cl2-containing plasma, with the objective of understanding the relationship between plasma characteristics and the competition between wall deposition of etch by-products and the creation of volatile etch by-products that flow into the downstream. The ICP was characterized by in-situ ion and neutral mass spectrometers, a chamber wall-mounted quartz crystal microbalance, optical emission spectroscopy, a wall-mounted ion flux probe, and an FTIR spectrometer in the turbomolecular pump foreline. Ru films were etched from 150 mm diameter wafers placed on a rf-biased substrate. Ru can be etched readily by Ar and O2-containing plasma. Cl2 addition results in significant changes in etch rate, wall deposition behavior, and downstream etch product composition. With 10 sccm Ar and 10 sccm O2 at 10mT pressure and 100V bias voltage, a 60 angstroms/min etching rate was observed. In addition, without Cl2 addition, no RuO4 was observed in the foreline, and almost all etch by-products were deposited on the chamber wall. With Cl2 addition (Ar/O2/Cl2 plasma), the etching rate increased by a factor of 5, RuO4 was observed downstream by FTIR, and virtually zero wall deposition rate was observed. One interpretation of the observations is that chlorine addition to the Ar/O2 plasma results in a more volatile Ru-oxychloride etch product, increasing both film etch rate and chamber wall re-etch rate.

9:40am **PS2-TuM5 Ru Etching Characteristics in Capacitively Coupled Ar/Cl@sub 2@/O@sub 2@ Plasma***, **S. Rauf**, P.L.G. Ventzek, V. Vartanian, B. Goolsby,* Freescale Semiconductor*; S. Burnett,* International Sematech*; L. Chen,* Tokyo Electron America Inc.

As the semiconductor industry attempts to replace the traditional gate dielectric, SiO@sub 2@, with higher-@kappa@ dielectrics (e.g., HfO@sub 2@), a thin metal layer need to be introduced in-between poly-silicon and gate dielectric to control conductor-dielectric interface properties. Ru is one metal that is being considered for this application. Along with electrical characteristics, the metal etching properties and compatibility of metal etch chemistry with other materials will determine how suitable a particular metal is for use in transistor gates. This paper describes a combined experimental and computational modeling investigation of Ru etching characteristics in a commercial dual frequency capacitively coupled Ar/Cl@sub 2@/O@sub 2@ plasma. Experiments explored the impact of gas mixture, RF power, gas pressure, and wafer temperature on Ru etch rate. Fourier transform infrared spectroscopy was also used to analyze effluents downstream from the plasma. Computational modeling was done using Io, a 2-dimensional plasma equipment simulation code. Plasma modeling results and blanket wafer etch rates were used to put together the Ru etch mechanism. Results indicate that reactive ion etching is the dominant Ru etch process, where O is first absorbed on Ru surface (generating RuO@sub x@) and the resulting compound is sputtered by energetic ions. The model captures experimental etch rate trends well at low gas pressures, but there is disparity between model and experiment at higher pressures. This difference is likely due to thermalization of sputtered Ru and RuO@sub x@ in the plasma, whose plasma chemistry is not well understood and, therefore, not accurately captured in our plasma chemical mechanism.

10:00am **PS2-TuM6 An Isotropic SiGe Etch Process for Fabrication of Silicon-on-Nothing Transistors***, **T. Sparks**, S. Rauf,* Freescale Semiconductor, France*; G. Cunge, L. Vallier,* LTM-CNRS, France

As the device dimensions are shrinking, the development of new transistor structures is essential to meet the ITRS roadmap device performance specifications. One such device, the Si-on-nothing (SON) transistor, utilizes a sacrificial SiGe epitaxial layer underneath a thin transistor active channel region. The SiGe layer is removed using a lateral isotropic etch process. Isotropic chemical downstream etch processes for SiGe removal suffer from high etch rates, low selectivity to Si and lack of insitu monitoring processes such as optical emission analysis. An alternative approach for lateral SiGe etching has been developed utilizing an inductively coupled plasma (ICP) operating in the 'remote' plasma mode, and it is described in this presentation. The etch process was designed using a combination of computational modeling and experiments. The Hybrid Plasma Equipment Model (HPEM) from the University of Illinois was utilized for plasma modeling and process design, and experiments in a commercial ICP reactor were used to confirm the predicted conditions. The plasma model was also coupled to a string-based feature scale model, where the etch mechanism was based on blanket wafer etching experiments and information available in literature. Etching was conducted in CF@sub 4@ containing plasmas, which will generate SiGe etchants (e.g., F) as well as polymer precursors for Si (e.g., CF@sub 2@). Possible mechanisms were investigated to understand the observed high isotropic etch selectivity of SiGe to Si. Process modeling also identified an intermediate gas pressure regime where plasma was localized close to the inductive coils away from the substrate. If the plasma is operated in this gas pressure regime without RF bias, ion energy flux at the substrate was small while flux of neutral etchants and polymer deposition precursors was reasonable. The resulting SiGe process therefore offered good selectivity to Si and a controllable etch rate.

10:20am **PS2-TuM7 X-ray Photoelectron Spectroscopy Study on Walls Coatings and Passivation Layers Generated on Sidewalls Trenches during Shallow Trench Isolation Processes.***, **C. Maurice**, B. Pelissier, G. Cunge, O. Joubert,* LTM-CNRS, France

For IC technology where delineating ever-finer structures is critical, wafer-to-wafer reproducibility is essential. Inherent to plasma processes, the coatings deposited on the reactor walls can disturb reproducibility by influencing the plasma chemistry. Simultaneously to walls coatings formation, passivation layers issued from etch products are deposited on the sidewalls of the etched patterns. These passivation layers, mandatory in obtaining controlled profiles are dependent on reactor walls conditions. This study proposes an XPS analysis of both walls coatings and of the passivation layers deposited during Shallow Trench Isolation (STI) processes. First, using a simple piece of Al@sub2@O@sub3@ floating on top of a 200 mm diameter wafer, walls conditions have been simulated and the chemical composition of the walls coatings analyzed quasi in-situ after each etching steps of the process. Secondly, using the combined effects of geometrical shadowing (allowing the screening of photoelectrons coming from the bottoms of the patterns) and of electrostatic charging, the chemical composition of the passivation layers formed on feature sidewalls has been determined. Results validate the technique even in the case of STI etching where the passivation layers are very thick. Comparison between the results obtained on the final walls coatings and passivation layers reveals in both cases the formation of SiOCl layers and thus the important correlation between the two deposits. Comparison between SiO@sub2@ and Si@sub3@N@sub4@ hard masks is performed. The impact of CF@sub4@ addition in typical Cl@sub2@/O@sub2@ chemistries is also investigated.

10:40am **PS2-TuM8 The Control of Electrode Impedance, Gas-Injection and Wafer-Temperature Radial Profile and their Effects on Poly-Gate Etching Performance***, **M.H. Hagihara**, L.C. Chen, F.H. Higuchi, Y.T. Tsukamoto, K.I. Inazawa,* TEL*; T.T. Tatsumi, A.K. Kawashima,* Sony

The etch rate and CD radial uniformity can be effectively optimized by controlling the radial profile of the inlet gas, the plasma parameters and the wafer temperature. A 2-zone ESC is used to control the wafer temperature radial profile. The ion energy and electron density (n@sub e@) radial distribution are controlled by the wafer-electrode's VHF impedance. The variable impedance is achieved by a series LC circuit where a variable capacitor is used. SCCM POLY source-plasma is generated by 60MHz VHF power while the 13.56MHz wafer-bias accelerates the ions.

The passage of the 60MHz electron towards the wafer-electrode and hence, the n@sub e@ radial profile, is strongly effected by the wafer-electrode's 60MHz impedance. In addition to the wafer-electrode's 13.56MHz bias power, the ion energy is also effected by its 60MHz impedance. The etcher is also equipped with a 2-zone gas showerhead providing radial distribution control of the neutral species. Etch data were taken for 4 poly-gate steps: fluorocarbon-based BARC etching, fluorocarbon TEOS hard mask open, fluorocarbon-based high-dope poly etching and HBr-based poly etching. A radial SW (Surface Wave) probe is used to measure the radial n@sub e@ directly above the wafer at various 60MHz impedance settings. Etch rate, XSEM profile and top-down CD uniformity are also recorded for various VHF impedance settings, 2-zone gas injection ratios and various 2-zone ESC temperature settings. Provision of these additional control knobs significantly improve the uniformity of the etch results.

11:00am **PS2-TuM9 Process Diagnostics and Optimization in Plasma Etch Chambers Using In-Situ Temperature Metrology*, P. MacDonald,*** OnWafer Technologies, Inc.*; B. Hatcher, J.P. Holland,* Applied Materials, Inc.*; M. Welch, M. Kruger,* OnWafer Technologies, Inc.

Performance metrics in plasma etching are strongly affected by various interacting mechanisms including direct chemical reaction, reactive etching, deposition, and mask erosion. Some of these basic etch mechanisms are extremely sensitive to temperature. As a result, across-wafer temperature variations are a first order indicator of etching performance in advanced plasma etch reactors. This temperature variation is a combination of effects ranging from reactor design to individual recipe parameters. With wafer-level thermal data available, any of these factors can be modified to improve process performance. This paper establishes concrete methodologies for in-situ process optimization using a wireless sensor system. The sensor system provides the precision necessary to break the ITRS "brick-wall" of "measurement precision of wafer surface temperature,"@super1@ by combining in-situ plasma SensorWafers and an advanced diagnostic data processing suite. This paper offers multiple examples on advanced polysilicon processes that illustrate rapid, effective process optimization and ESC diagnostics. In the process optimization section, state-of-the-art polysilicon etch chambers are evaluated for critical process characteristics. The effectiveness of temporal/spatial temperature signatures as indicators of process performance is demonstrated. Wafer-level thermal data is correlated to actual device results to verify performance of the optimized process. In the ESC characterization segment, multiple leading-edge ESC designs are evaluated to ensure process transferability and performance. The effectiveness of temporal/spatial temperature signatures to quickly and easily evaluate ESC design iterations is demonstrated. These diagnostics save considerable time and effort over the current methods established for ESC fingerprinting. @FootnoteText@ @footnote 1@ ITRS: 2003, Table 6, Key Sensor Technology Requirements.

11:20am **PS2-TuM10 New Mthod to Analyse Chamber Walls Coating during Plasma Etch Processes*, O. Joubert,*** *G. Cunge, B. Pelissier, C. Maurice, L. Vallier,* LTM-CNRS, France

In today's etching processes for microelectronic application the shape of the etched feature must be controlled within 5 nm. This nanometer-scale linewidth control requires a perfect process repeatability. In high density plasmas operating at low pressure it is difficult to achieve due to the deposition of organic (or mineral) layers on the reactors walls during the process. This formation of this layer on the reactor walls modifies the surface loss probability and the concentrations of radicals involved in the etching process, leading to process instabilities. However, the chemical nature of these layers, their deposition mechanism and their influence on the plasma chemistry remains poorly understood. Recently, we have developed a new and very simple method based on the fact that a small piece of Al@sub 2@O@sub 3@ floating on top of a 200 mm diameter wafer during an etch process experiences the same exposition to the plasma than the chamber walls. We have then use quasi in situ XPS measurements to have access to the chemical nature of the layers formed on the floating Al@sub 2@O@sub 3@, i.e the chamber walls, during plasma etching processes. Using this technique, we can determine accurately the chemical nature of the layers coated on the reactor walls after various etching processes including silicon and metal (TiN) gate etching. We will demonstrate that the final nature of the chamber wall coatings is strongly influenced by the presence of resist on the wafer, nature of the layers composing the gate stack and chemistries used during the different steps of the process. We will then discuss the cleaning strategies that are commonly used after gate etching processes and their limitations.

Tuesday Afternoon, November 16, 2004

MEMS and NEMS
Room 213C - Session MN+MS+PS+TF-TuA
Nano/MEMS Manufacturing and Plasmas

Moderator: R. Ghodssi, University of Maryland

1:20pm **MN+MS+PS+TF-TuA1 Wafer-Level, Low-Cost, High-Vacuum Packaging of MEMS Devices Using Nanogetter TM**, ***N. Najafi***, *D.S. Sparks,* Integrated Sensing Systems, Inc. (ISSYS) **INVITED**

As part of its development effort to commercialize a Micro-Density Meter, ISSYS Inc. invented a new technology for long-term, low-cost, wafer-level, high-vacuum, hermetic encapsulation of MEMS devices. This technology is now commercially available through a spin-off company: Nanogetter Inc. At the system level perspective, one of the most attractive features that NanogetterTM offers to the MEMS community is a "Total Solution" to an important problem facing many emerging MEMS products. Nanogetters Inc. technology offers: Wafer-level, high-vacuum (< 1mTorr) encapsulation, Long-term vacuum stability, Hermetic electrical lead transfer, Compatibility with all MEMS technologies (polysilicon surface, bulk, silicon-on glass, and LIGA micromachining technologies), High yield, Low cost In addition to high-vacuum packaging applications, NanogetterTM will be further developed to provide ambient environments suitable for applications requiring higher pressures. For example, for micro-switches and accelerometers, the technology will absorb humidity and oxygen. As a testbed for using this wafer-level, high-vacuum technology, the performance of a micro-density meter will be presented.

2:00pm **MN+MS+PS+TF-TuA3 Low-Pressure and Plasma-Enhanced Chemical Vapor Deposition Modeling at the Feature Length Scale of MEMS Devices**, ***L.C. Musson,*** Sandia National Laboratories; *P. Ho,* Reaction Design; *R.C. Schmidt,* Sandia National Laboratories

Theoretical modeling of the surface chemistry and concomitant surface evolution during MEMS fabrication processes has great potential for improving surface micromachining (SMM) process technologies. A greater understanding of the fundamental factors leading to surface non-uniformities and other non-ideal geometric artifacts can lead to better device designs and assist in process optimization. We are developing ChISELS, a parallel code to model material deposition and etch processes at the feature scale. ChISELS uses the level-set method which was chosen for its natural ability to handle substantial changes in topology that occur when fabricating MEMS devices. We describe the algorithm by which the surface is evolved in process models, the transport model, the tools used for modeling chemical reactions and dynamic balancing of the computational load in a parallel environment. The capabilities of the ChISELS code are demonstrated by models of low-pressure deposition of SiO2 from TEOS and from a silane/oxygen/argon plasma. The uniformity of deposition into various geometries has been studied and will be presented in both 2-D and 3-D models. Some comparisons between the predicted deposition geometries and experimental SEMs will also be shown.

2:20pm **MN+MS+PS+TF-TuA4 Detection of Metal Film Deposit Smoothness by a MEMS-NEMS Structure via Surface Plasmon Effects**, ***D.T. Wei,*** Wei & Assoc.; *A. Scherer,* California Institute of Technology

A thin metal film under strong illumination, from uv to visible, will induce a quantum effect of electron plasma called surface plasmon effect. When the film is a deposit on a semiconductor surface, it takes additional structure in submicron scale to make an electronic detector. This detection method has high potential for controlling the smoothness of metal coating by traditional plasma or by ion beam deposition. Such an integrated structure is effective to detect the surface roughnesses vs. plasmon modes not often obtainable through other means, such as their decay products. A NEMS device is designed and fabricated for collecting electrons from the decaying surface plasmons in avalanche mode. The signal responds to the degree of the metal deposit surface roughness down to nano, even subnano sizes. Imperfections in metal film resulted from thermal plasma deposition are theoretically analyzed and relevant data are presented from the nano structure with new insights. Assembled unit will be applicable to monitoring the metal coating smoothness. Applications in transparent electroding and adaptive optics are sought.

2:40pm **MN+MS+PS+TF-TuA5 Etching of High Aspect Ratio Structures in Si using SF@sub 6@-O@sub 2@-HBr and SF@sub 6@-O@sub 2@-Cl@sub 2@ Plasmas**, ***S. Gomez,*** *J. Belen,* University of California, Santa Barbara; *M. Kiehlbauch,* Lam Research Corporation; *E.S. Aydil,* University of California, Santa Barbara

Plasma etching of high aspect ratio (depth-to-width) structures in Si is a crucial step in manufacturing trench capacitors for memory devices, and integrated components for microelectromechanical systems (MEMS). We have investigated etching of deep (~3-10 µm) and narrow (~0.2-0.5µm) features with high aspect ratios (~10-50) using plasmas maintained in mixtures of SF@sub 6@, O@sub 2@ and HBr gases, and in mixtures of SF@sub 6@, O@sub 2@ and Cl@sub 2@ gases as an alternative to the Bosch process. Experiments were conducted in a low pressure (25 mTorr), high density, inductively coupled plasma etching reactor with a planar coil to maintain the discharge and with radio frequency (rf) biasing of the substrate electrode to achieve independent control of the ion flux and ion energies. Specifically, we have studied HBr and Cl@sub 2@ addition to SF@sub 6@/O@sub 2@ plasmas and O@sub 2@ addition to SF@sub 6@/HBr and to SF@sub 6@/Cl@sub 2@ plasmas. We have analyzed the effect of these additions on the etch rate and feature profile using Si wafers patterned with 0.2 µm diameter holes in a SiO@sub 2@ mask. Visualization of the profiles using SEM is complemented by plasma diagnostics such as optical emission and mass spectroscopies to understand the key factors that control the anisotropy and etch rate. Upon adding HBr to an SF@sub 6@/O@sub 2@ plasma, a silicon oxybromide film forms on the sidewall, reducing undercut and increasing taper. However, subsequent reduction of O@sub 2@ gas increases mask undercut and isotropic etching by reducing sidewall oxidation. On the other hand, adding Cl@sub 2@ to an SF@sub 6@/O@sub 2@ plasma causes a reduction of O density and a weak silicon oxychloride film forms on the sidewall. This chlorinated film is more easily etched by F, therefore increasing mask undercut. Subsequent reduction of O@sub 2@ gas further increases mask undercut and isotropic etching.

3:00pm **MN+MS+PS+TF-TuA6 Deep Reactive Ion Etching of Silicon Structures for Profile and Morphology Control**, ***R.J. Shul,*** *M.G. Blain, S.G. Rich, S.A. Zmuda,* Sandia National Laboratories

Deep reactive ion etching (DRIE) of Si or the Bosch process relies on an iterative etch/deposition process where a sidewall etch inhibitor is formed to prevent lateral etching of the Si thus resulting in highly anisotropic etch profiles at reasonably high etch rates. The formation of deep, high-aspect ratio, straight-wall Si structures achieved with this process has been used to fabricate chemical and biological sensors, micro-fluidic devices, and mechanical actuators and gears. However as device designs become more complicated and aspect ratios increase, conventional DRIE processes often cannot meet the demands. For example, high-aspect ratio features etched to depths greater than 150 microns often become tapered and rough with unacceptably slow etch rates. This observation is often referred to as RIE lag or aspect ratio dependent etching and is attributed to reduced diffusion of neutral reactants and etch product species and reduced ion transport to the feature bottom as the depth increases. In many cases the etch will actually terminate due to either inefficient etching or polymer deposition dominating the process. We will report on the use of the DRIE platform to fabricate deep, high-aspect ratio Si features incorporating a process in which etch parameters are incrementally varied during each cycle of the process. The use of this in-situ variable etch process has resulted in a high degree of profile control and smooth etch morphologies while maintaining reasonably fast etch rates for high aspect ratio features. Etch results using this process will be reported as a function of cathode power, etch and deposition time, and reactive gas flow. These results will be compared to results obtained using conventional DRIE processes. Sandia is 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.

3:20pm **MN+MS+PS+TF-TuA7 Fabrication of Wide-IF 200-300 GHz SIS Mixers with Suspended Metal Beam Leads Formed on SOI**, ***A.B. Kaul,*** *B. Bumble, K.A. Lee, H.G. LeDuc,* Jet Propulsion Laboratory, California Institute of Technology; *F. Rice, J. Zmuidzinas,* California Institute of Technology

We report on a novel fabrication process that uses SOI substrates and micromachining techniques to form wide-IF SIS mixer devices that have suspended metal beam leads for RF grounding. The mixers are formed on thin 25 µm membranes of Si, and are designed to operate in the 200 - 300 GHz band. Potential applications are in tropospheric chemistry, where increased sensitivity detectors and wide-IF bandwidth receivers are desired. They will also be useful in astrophysics to monitor absorption lines

for CO at 230 GHz, to study distant, highly red-shifted galaxies by reducing scan times. Aside from a description of the fabrication process, electrical measurements of these Nb/Al-AlNx/Nb trilayer devices will also be presented. Since device quality is sensitive to thermal excursions, the new process appears to be compatible with conventional SIS device fabrication technology.

3:40pm **MN+MS+PS+TF-TuA8 Characterization of Polycrystalline AlN Film Quality Using Variable Angle Spectroscopic Ellipsometry***, **L.-P. Wang**, D.S. Shim, Q. Ma, V.R. Rao, E. Ginsburg, A. Talalyevsky,* Intel Corp

Aluminum nitride (AlN) thin films have been investigated for piezoelectric, wide band gap, high-k dielectric and other applications. Recently, AlN films for bulk acoustic wave (BAW) resonators and filters have been studied extensively, driven by the fast growth of wireless communications. For this application, AlN films are mostly prepared by reactive sputtering, a technique with the advantage of low deposition temperature, easy process control and low cost when compared to alternatives such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). Highly c-axis oriented AlN films are desirable for optimal piezoelectric and crystal properties. Currently, X-ray diffraction (XRD) rocking curve is the predominate method for characterizing the crystal and piezoelectric properties. In this study, optical constants of AlN films, refractive index (n) and extinction coefficient (k), were determined by a variable angle spectroscopic ellipsometry (VASE). The microstructure of the sputtered polycrystalline films is well reflected in the VASE optical model, which includes cylindrical symmetry, effective medium approximation (EMA), index gradient, and surface roughness. For the first time, the film optical constants were correlated to the full width at half maximum (FWHM) of XRD rocking curve. It was found that the films with smaller FWHM, an indication of better crystal and piezoelectric properties, had higher n and lower k. This is consistent with the general observation that higher n and k of polycrystalline films typically have fewer defects and better microstructures. The correlation between the optical parameters and the film quality leads to a simpler and faster method for characterizing sputtered AlN films. Furthermore, such optical tools can be integrated in a sputter deposition system for in-situ monitoring of AlN film thickness and quality simultaneously.

Plasma Science and Technology
Room 213A - Session PS+MS-TuA
45nm Node with Panel Discussion

Moderators: B. Ji, Air Products and Chemicals, Inc., G. Oehrlein, University of Maryland

1:20pm **PS+MS-TuA1 Preliminary Investigations for Ultimate Gate Patterning***, E. Pargon,* LTM-CNRS, France*; **J. Foucher**,* CEA-LETI, France*; J. Thiault, O. Joubert,* LTM-CNRS, France

The fabrication of a sub-20nm transistor gate requires a very accurate control and understanding of all the plasma steps (resist trimming, BARC, hard mask open and gate etch) involved in the gate stack processes. Then, it is important to study the parameters that can generate a deviation of the final gate dimension for each of these plasma steps. The two aspects that we have studied are the etching behaviour of the photoresist mask exposed to the plasma, and the chemical nature of the layers that deposit on the reactor walls and feature sidewalls during the process. We have developed an experimental procedure using XPS analyses to characterize the chemical modifications occurring on the tops and sidewalls of the photoresist mask as well as the chemical nature of the coatings formed on the chamber walls. These analyses can be correlated with the process performances (in terms of etch profile and critical dimension control (CD control). SEM observations and CD AFM 3D have been used to get the process performance. In all the plasma conditions investigated, the BARC and hard mask opening steps both lead to a CD deviation of 5 to 15 nm attributed to the modifications of the photoresist mask during plasma exposure. XPS analyses and 3D AFM measurements show that the passivation layers formed on the pattern sidewalls during the gate etch step itself are strongly influenced by the pattern density and etch chemistry. Finally, we show that the only way to control gate etch processes in the sub 20 nm range is to minimize strongly the formation of the passivation layers on the gate sidewalls.

1:40pm **PS+MS-TuA2 EUV Light Source Development and Debris Mitigation For 45nm Node Lithography and Beyond***, **B.E. Jurczyk**, M.A. Jaworski, M.J. Neumann, M.J. Williams, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Discharge-produced plasma (DPP) light sources are leading candidates for generating 13.5-nm wavelengths needed for next-generation optical lithography. Traditional DPP sources have used xenon radiators due to its cleanliness; however, high output requirements (>115W at first focus) are driving developers towards higher conversion efficiency fuels such as tin. As a result, condensable tin vapor and electrode debris reaching and damaging the first collector optic is a serious concern for device lifetime and cost of ownership. A secondary-plasma debris mitigation technique was successfully demonstrated for noble gas light sources at the Illinois Debris-mitigation EUV Applications Laboratory (IDEAL). The IDEAL facility utilizes a dense plasma focus discharge source operating at nominal conditions of 15 J/pulse, 50 Hz rep rate, and 3 kV. Electrode sputtered debris is re-ionized in a secondary plasma region and removed with a biased foil trap prior to the collection optics. For a low density plasma (10@super 9@ cm@super -3@) condition, a debris removal fraction of 61% ± 3% was observed. The experimental chamber has been modified to operate with tin delivery into the pinch region. Results from electrode redesign, tin injection, EUV light output and condensable tin vapor mitigation will be presented. High density results from an improved internal helical-resonator shielded inductive coil configuration give greater protection efficiency. Fast ions contributing to optic erosion have been observed. Results from a gridded energy analyzer shows two peaked ion distributions at 2.8 keV and 5.8 keV. Elevated plasma potential and sheathing effects have shown an increase in ion energy at the boundaries. An improved ESA/TOF system provides < 5 eV spectral energy resolution and information on charge/mass ratio. Preliminary results from the new Surface Cleaning of Optics by Plasma Exposure (SCOPE) facility are presented for advanced fuel interactions on optical components.

2:00pm **PS+MS-TuA3 Fundamental Studies on Low-k Processing***, **T. Tatsumi**,* Sony Corporation, Japan **INVITED**

The need for reliable low-k/Cu interconnect technologies is increasing, and many kinds of low-k materials have been proposed. We need a process design for etching that will correspond to a change in the film densities and compositions of low-k materials for 90 and 65-nm node devices. Using many different in-situ plasma-measuring tools, such as IRLAS, OES, surface wave probes, and QMS, we counted the absolute number of incident species (CF@sub x@, O, N, H, F, radicals and ions) that were dissociated and/or ionized in fluorocarbon plasmas. Next, we evaluated the surfaces of the various SiOCH films (k = 2.9-2.2) that had different film compositions and densities, and that had been exposed to various fluorocarbon plasmas. The etch rates, selectivity, and thicknesses of the surface polymers were analyzed. We found that the etch rates of the SiOCH films depended on both the "total number of F atoms in all of the incident CF@sub x@ reactive species", and "the surface reaction probability, which depends on ion energy". Lower oxygen concentrations in SiOCH film induce a narrower process window because the fluorocarbon polymer became thicker, even during lower incident CF@sub x@ flux conditions.@footnote 1@ As a result, the etch rate became very sensitive to changes in the incident CF@sub x@ fluxes, resulting a narrow process window for etching SiOCH and porous SiOCH materials. To ensure reliable interconnects for 45 nm and beyond, we require new technologies to realize both "quantitative control" and "instant stabilization" of the plasma parameters. Furthermore, we also need to develop a model to control the atomic layer modification (etching and/or degradation) of the actual etched surface for various materials. Cooperation between etching and other unit process engineers must be promoted in order to create a more reliable process module. @FootnoteText@ @footnote 1@ T.Tatsumi et al, Proceedings of the 2003 IITC (2003) 239.

2:40pm **PS+MS-TuA5 Plasma Etch Challenges for 45 nm Node and Beyond***, **R. Wise**,* IBM **INVITED**

Many novel technologies are candidates for introduction at the 45 nm technology node. Metal gate electrodes, high-k gate dielectric materials, hybrid oriented transistors (HOT), FINFET transistors, new silicide materials, multiple stressed liners, fully-silicided gates, and porous low-k BEOL materials are all currently under evaluation for introduction at the 45 nm node. The anticipated impact of each of these technology components on requirements of dry etch process and tooling is discussed in detail. Lithographic limitations will continue to require dry etch processes (e.g. gate, contact) to provide additional CD reduction to meet designed groundrules. These processes will include extension of well-known resist

trim techniques as well as other techniques, such as providing a controllable taper through a sacrificial masking material. Available resist material will be reduced both by limitations of the lithographic process window (N.A , DOF, resolution) as well as implementation of multiple exposure techniques. These reductions in the available mask thickness required to preserve lithography process window have driven the need for highly selective etch processes, generally at the expense of uniformity (especially on 300 mm wafer sizes), defectivity, and profile of the transferred pattern. Later generation lithographic materials are expected to continue to exhibit increased sensitivity to line edge roughness. Process and tooling needs required to address these lithographic challenges are discussed.

3:20pm **PS+MS-TuA7 Invited Panel - "Challenges for 45 nm Node"***, C. Gabriel,* AMD (damage)*; M. Hussein,* Intel (scaling)*; C.-J. Kang,* Samsung (dielectric etch)*; S. Wege,* Infineon (silicon etch)

Panelists will present 5-minute perspectives.

3:40pm **PS+MS-TuA8 Discussion - "Challenges for 45 nm Node" Panelists and Attendees***,*

Plasma Science and Technology
Room 213B - Session PS2-TuA
Plasma and Polymers

Moderator: L.J. Overzet, University of Texas at Dallas

1:20pm **PS2-TuA1 Plasmas, Polymers and Plasma-deposited Polymer-like Films: Plasma Diagnostic Studies for SiO@sub 2@-like Film Deposition***, M. Creatore,* ***M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands **INVITED**

Low temperature plasmas for polymer modification and synthesis of polymer-like films are technologically appealing because of the development of plastic-based applications and the versatility of plasmas as processing tool in engineering the polymer-like film. As plasmas invade hot topics such as flexible electronics and nano-scale devices, the plasma-based technology urgently needs the support of fundamental studies, which can unravel the mechanisms of plasma-polymer interactions and deposition of polymer-like films. A valid example is the deposition of SiO@sub 2@ barrier layers on polymers for long-term stability devices, such as plastic windows, polyLEDs and TFTs: here the requirement of water vapor permeability is more demanding that in food packaging. This involves issues, such as the development of an interphase and the generation of defects during film growth, which go beyond the recipe for a stoichiometric, dense SiO@sub 2@ layer. Another example is the deposition of SiC@sub x@H@sub y@O@sub z@ polymer-like films as low-k dielectrics for ULSI technology. Highlighting the monomer dissociation paths is not only useful in controlling the carbon content in the film and, therefore, the quality of the dielectric, but it is also expected to pave the way towards the engineering of ultra-low-k materials. This contribution describes, through the chosen model system of SiO@sub 2@ and SiC@sub x@H@sub y@O@sub z@ film deposition, studies performed in an Ar-fed remote expanding thermal plasma where O@sub 2@ and hexamethyldisiloxane are injected downstream. The monomer dissociation paths controlled by the (Ar@super +@, e@super -@) flow emanating from the plasma source will be discussed in view of the results obtained by Cavity Ring Down Spectroscopy and Triple Stage Threshold Ionization Mass Spectrometry. Implications of these outcomes on the plasma-deposited film properties will be also addressed.

2:00pm **PS2-TuA3 Deposition of SiOx Films from Organosilicone and Oxygen Plasma under Continuous and Pulsed Modes***,* ***S.R. Kim,*** Chungju National University, Korea, South Korea

RF plasma enhanced chemical deposition were applied to get SiO@sub x@ on polymeric substrates with various processing conditions, such as input power, monomer/oxygen feed ratio, modulated frequency and duty cycle. Organosilicones were used as feed monomer and oxygen was used as mixing gas. Input power was varied from 50 to 300 Watt. Chemical bonding information of deposited film by FTIR-ATR shows that the absorption peak of Si-O near 1032 cm@super -1@ moved toward 1066 cm@super -1@ and Si-CH@sub 3@ peak was decreased as oxygen amount was increased. I-V curves from Lanmuir Probe was used to measure electron temperature, electron density and plasma potential. Optical Emission Spectroscopy (OES) was used to measure the plasma species and intensity of species and to obtain plasma pathway. Plasma density was of 4 x 10@super 8@ [cm@super -3@] and electron temperature of 2.8 eV and maximum deposition rate was 640 Å/min at 150 Watt. Plasma parameters, such as electron temperature, electron density, plasma potential, and plasma species were correlated to the properties of deposited films.

2:20pm **PS2-TuA4 Electron Impact Reactions of DVS-BCB Monomer in He Plasma for Low-k Film Deposition***,* ***K. KINOSHITA****, M. SHIMOYAMA, A. NAKANO, J. KAWAHARA, N. KUNIMI, T. KIKKAWA,* Mirai, Japan

DVS-BCB (divinylsiloxane-bis-benzocyclobutene) is known as a precursor of a spin-on low-k material with the dielectric constant of 2.7@footnote 1@. Plasma polymerization process has also been developed to deposit DVS-BCB film from the monomer@footnote 2@. Higher thermal stability (400 °C) and very thin (<20 nm) conformal film formation have been achieved by this vapor phase deposition technique. However, reactions of DVS-BCB in the plasma remain unclear. Recently, in-situ quadrupole mass spectrometry (QMS) study of this plasma showed that there were two types of unique reactions which had never been observed in the thermal polymerization process@footnote 3@. These were hydrogen attachment to and methyl group desorption from the DVS-BCB, resulting in different polymer structures from those of thermally polymerized films. This paper reports molecular orbital calculations for these reactions. Total MO energy calculated by the density functional technique with the 6-31G* basis set clearly showed that both the neutral DVS-BCB and ionized DVS-BCB were stabilized by the hydrogen attachment. The attachment energies are about 2 eV and 4 eV for neutral and ionized species, respectively. The methyl group desorption was also analyzed by changing the Si-CH@sub 3@ distance. When the Si-CH@sub 3@ distance d was stretched from the stable position (d=1.88 Å), there appeared two types of saddle point structures at d=2.38 - 3.88 Å before final dissociation. The total MO energy at this final condition showed a lower value than the transition state. This means, methyl group desorption reaction needs activation to proceeds. The MO calculations well explain the QMS observations. This work was supported by NEDO. @FootnoteText@ @footnote 1@ T. M. Stokich, Jr., et al.: Mat. Res. Soc. Symp. Proc., 227, (1991) 103.@footnote 2@ J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2-1, (2003) 143.@footnote 3@ K. Kinoshita, et al., Proc. Dry Process Symp. 2003, 6-6, (2003) 157.

2:40pm **PS2-TuA5 Molecular Dynamics Study of Interactions Between Organic Polymer Surfaces and Hydrogen/Nitrogen Radical Beams***,* ***H.Y. Yamada,*** Kyoto University, Japan*; S.H. Hamaguchi,* Osaka University, Japan

We have studied atomistic scale interactions between organic polymer surfaces and beams obtained from hydrogen/nitrogen plasmas, using classical molecular dynamics (MD) simulations. In typical etching processes of low-dielectric-constant (i.e. low-k) organic polymer layers for semiconductor interconnect applications, hydrogen and nitrogen based plasmas are often employed as their plasma etching sources. To carry out MD calculations of such systems, we have developed a classical interatomic potential model for systems consisting of H, C and N atoms, using interatomic potential data obtained from quantum mechanical calculations. One of the key factors that allow us to appropriately handle various covalent bonds formed among C and N atoms in numerical simulations is an algorithm that we have developed to determine the order of each covalent bond automatically based on local atomic arrangement. In this presentation, we shall discuss details of the newly developed potential model as well as sample MD simulations. As to MD simulations, we have focused on plasma etching of low-k organic polymer surfaces and simulated interactions of such polymer surfaces with energetic radical/cluster beams containing N and/or H atoms. The results obtained from these MD simulations are also compared with recent experimental observations as well as previously obtained MD simulation results for hydrocarbon beam injections into organic polymer surfaces [H. Yamada and S. Hamaguchi, J. Appl. Phys. (2004), submitted.]. We have observed that, as in the case of carbon beam injection simulations, injected N atoms strongly react with the polymer substrate and form bonding networks of C and N atoms on the substrate surface. On the other hand, at similar low injection energies, N2 molecules are less reactive due to their strong covalent bonds. At higher injection energies, however, we have observed that more N molecules can break into N atoms and form bonding networks on the polymer substrate.

3:00pm **PS2-TuA6 Computational Investigation of the Role of Polyatomic Ions in Plasma Polymer Deposition***, I. Jang, W.-D. Hsu,* ***S.B. Sinnott****,* University of Florida

Fluorocarbon plasmas are widely used to chemically modify 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. For this reason, the deposition of mass selected fluorocarbon ions are useful for isolating the effects specific to polyatomic ions. In this study, the detailed chemical modifications that result from the deposition of beams of polyatomic fluorocarbon ions (C@sub 3@F@sub 5@@super +@ and CF@sub 3@@super +@) on polystyrene surfaces at experimental fluxes are identified using classical molecular dynamics simulations with many-body empirical potentials. The ions are deposited at incident energies of 50 or 100 eV/ion. For CF@sub 3@@super +@ deposition, F atoms play the most important role in fluorinating the polystyrene surface, as the majority of F atoms are covalently attached to the polymer chains through replacement of native H atoms or capping the ends of broken chains. CF@sub 2@ fragments are also an important long-lived species. In contrast, F atoms are a minor bi-product and CF@sub 2@ fragments are the most dominant species for C@sub 3@F@sub 5@@super +@ deposition on polystyrene. Thus the simulations explain the experimental finding that C@sub 3@F@sub 5@@super +@ is more efficient at producing fluorocarbon thin films. In particular, many larger fragments produced by C@sub 3@F@sub 5@@super +@ ion deposition contain more than one C atom, may have more than one active site, and readily react to grow polymer-like structures. In contrast, F atoms, the most dominant fragment in CF@sub 3@@super +@ deposition, effectively deactivate potential film nucleation sites when they fluorinate the polymer surface. We compare these findings to results for the deposition of comparable hydrocarbon ions (C@sub 3@H@sub 5@@super +@ and CH@sub 3@@super +@). This work is supported by the National Science Foundation (CHE-0200838).

3:20pm **PS2-TuA7 Study of the Selected Effect of Molecules Generated in N@sub 2@ and O@sub 2@ Plasma for the Surface Modification of HDPE, PVDF and PTFE.**, *N. Vandencasteele,* Universite Libre de Bruxelles, Belgium*; A. Wagner,* Ames National Laboratory*; H. Fairbrother,* Johns Hopkins University*; **F. Reniers,*** Universite Libre de Bruxelles, Belgium

Although plasma treatments of polymers are widely used in today's industry, the surface modification mechanisms remain mostly unknown due to their complexity. The wide variety of the species generated in a plasma, combined with the specificity of a usual polymer surface make such reactions hard to understand. We have undertaken a global systematic study of the individual and synergetic effects of the species generated in a plasma on the surface modification of a series of model polymers: HDPE, PVDF, PTFE, as they illustrate the transition between C-H and C-F bonds. A modified RF plasma allowing to filter out some of the species was used@footnote 1@, as well as an in situ ion gun and a radical source. N@sub 2@ and O@sub 2@ plasmas were used, and the selected effect of N@sub2@@super +@/N@super +@, O@sub 2@@super +@/O@super +@ and O on the polymers was studied. Samples were characterized using water contact angle (WCA), AFM and XPS. The spatial distribution of the plasma species was analysed by OES. In our configuration, most of the particles reaching the polymer are neutrals and electrons. Results show that the nature and amount of the functionalities grafted, the roughness and the WCA strongly depend on the starting polymer, and on the nature of the incident beam. For instance, the functions grafted on HDPE using the plasma neutrals are mostly C=N groups, whereas nitrogen ion treatment leads to a majority of amines. The N@sub 2@ plasma treatment of PTFE induces defluorination of the polymer, with rapid increase of the nitrogen content. New chemical functions, and CF@sub 3@ groups are evidenced. The decrease of the WCA is directly correlated to the surface amount of nitrogen. On the contrary, exposure of PTFE to N ions leads to no significant grafting. Oxygen treatment of HDPE and PVDF lead to an increase of surface energy, but on PTFE a super-hydrophobic surface is created. @FootnoteText@ @footnote 1@ A. Wagner, D.H. Fairbrother, F. Reniers, plasma and polymers, 8 (2003) 119.

3:40pm **PS2-TuA8 Deposition of Plasma Polymer Coatings on Stainless Steel***,* ***A. Mistry,*** University of Sheffield, UK, U.K.*; F.R. Jones,* University of Sheffield, UK*; D.B. Hammond, T.H. English,* Corus Plc. Rotherham, UK

Plasma polymerisation is being investigated to produce coatings imparting a specific function on the surface of stainless steels, such as improved cleanability. One approach to this goal is through deposition of inorganic oxide layers that enhance the hydrophilicity of the surface, improve water run-off properties and enhance the surface's dirt shedding properties. Preliminary work with hexamethyldisiloxane (HMDSO) and titanium containing organo-metallic monomers, e.g. titanium (IV) isopropoxide, as the precursor with/without O@sub 2@ as a co-reactant for plasma polymerisation onto stainless steel has shown the potential of this approach. The results from XPS indicate that as the concentration of O@sub 2@ in the plasma increases, the species deposited on the surface incorporate less carbon. There is also a decrease in the measured contact angle, i.e. the surface becomes more hydrophilic. This change in surface chemistry to a more oxide-like state is shown by an increase in O:Metal ratio. Thus, the surface chemistry can change from organic polymeric-like at high monomer concentration and low power, to inorganic oxide-like at low monomer concentration and high power. The cleaning response of the coated surfaces has been investigated, and copolymerisation of these two monomers to impart other synergistic effects is being carried out.

Plasma Science and Technology
Room Exhibit Hall B - Session PS-TuP

Poster Session

**PS-TuP1 CVD Chamber Cleaning by F2 Remote Plasma Processing*, S.C. Kang*, *J.Y. Hwang, N.-E. Lee,* Sungkyunkwan University, South Korea*; K.S. Joo, G.H. Bae,* Shihwa Indus. Com, South Korea

Cleaning of chemical vapor deposition (CVD) chamber during the deposition of SiO @sub 2@, Si @sub 3@N@sub 4@, Si, and W thin films in Si device manufacturing fabs has been carried out using perfluorocompounds (PFCs) including C @sub 2@F@sub 6@, NF @sub 3@, C @sub 3@F@sub 8@, and C @sub 4@F@sub 8@ etc. During CVD chamber cleaning using PFCs, effect of re-emitted PFCs on global warming and difficulty of cleaning the silicon oxide layers have been of great concern. F @sub 2@ cleaning is expected to get rid of the global warming effect completely and contribute to a reduction of operating costs by the use of on-site F @sub 2@ generation systems. However, adoption of F @sub 2@ CVD chamber cleaning has been limited due to high toxicity and reactivity of F @sub 2@ gas. In this study, we carried out CVD chamber cleaning experiments by F@sub 2@ remote plasma generated from a toroidal-type remote plasma source in a commercial 8-inch plasma enhanced chemical vapor deposition (PECVD) system. In this experiment, bottled F @sub 2@ gas was used. Due to difficulty of handling F @sub 2@ gas, various safety measures for storage and delivery were made. Chamber cleaning experiments of silicon oxide layers including PE-TEOS and BPSG were carried out by varying the F @sub 2@ /Ar gas flow ratio, flow rate, pressure, and temperature. Species emitted during cleaning were monitored by Fourier transformed infrared spectroscopy (FT-IR) and residual gas analyzer (RGA). Under the current experimental condition, cleaning rate was increased with F @sub 2@ gas flow rate increased. Destruction removal efficiency (DRE) of F @sub 2@ gas was calculated by evaluating the emitted F @sub 2@ gas during cleaning using residual gas analysis. Effect of various process parameters on cleaning process will be discussed in detail.

PS-TuP2 Design and Development of an Advanced Dielectric Etch Tool using Simulation*, K. Bera,* *Y. Ye, D. Hoffman, G.A. Delgadino, J. Carducci,* Applied Materials, Inc.

Creating a successful all-in-one (main etch, PR ash, and clean) chamber for dual damascene etch requires thorough understanding of the relationships among plasma density, ion energy, and distribution of charged and neutral species to achieve operational capability over a wide range of plasma density and ion energy at widely different pressures and gas flows. This paper presents several aspects of hardware design and process optimization for a 300mm etcher for 90nm technology and below in which simulation was used to gain insight into these phenomena. Plasma simulations demonstrated that higher frequencies generated denser plasma for a given power than lower frequencies, which focused the selection of source frequency for the reactor. Higher frequencies were shown to improve the dissociation fraction promoting creation of desirable facet-protecting polymers. Simulations further revealed that higher frequencies produced lower-energy, less potentially damaging ion bombardment to the wafer. Simulations guided effective chamber cleaning using source. Confinement ring design was optimized using plasma simulation that allowed us to confine plasma for clean mode operations. Flow simulation calculated chamber conductance guiding the chamber design for wide process window. Simulation showed that Neutral Species Tuning Unit (NSTU) can tune pressure and velocity uniformities, and hence CD-bias and profile uniformities. Separate control of plasma density and energy distribution from distribution of neutral and charged species within the chamber was used to demonstrate independent optimization of the etch rate and CD-bias uniformities for dual damascene trench etch process.

PS-TuP3 Spectroscopic Study of Effect of Wall Conditions on Gas Phase and Surface Phase Chemistries in Inductively Coupled Fluorocarbon Plasmas*, B.S. Zhou,* *E.A. Joseph, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

The effect of wall conditions including dimension, material, temperature, and cleanliness on the gas phase and surface phase chemistries in CF@sub 4@ plasma etching of Si was studied in the modified Gaseous Electronics Conference (mGEC) reference cell. In the mGEC, Al inner walls of various diameters were used to confine the plasma to the center of the chamber and induce changes in the gas phase chemistry. The range of the wall temperature was 25 -150°C. The gaseous molecules and radicals monitored included CF@sub 4@, CF@sub 3@, CF@sub 2@, SiF@sub 4@ and COF@sub 2@, among which CF@sub 4@ and SiF@sub 4@ were found to be the two dominant species, accounting for about 80% of the total concentration. The density ratio of SiF@sub 4@ and COF@sub 2@ was about 2:1 with no bias on the substrate and increased to ~6:1 when Si substrate etching took place. Specifically, as the Si etch rate increased, the COF@sub 2@ density dropped, likely due to suppressed etching of the quartz source window, while the density of SiF@sub 4@ increased. These rates are likely linked through the atomic fluorine density. In addition, the CF@sub 3@ radical density was observed to increase over time. This is indicative of increased surface production of fluorocarbon species from CF@sub x@ film on the wall. This work is supported by a grant from NSF/DOE, CTS-0078669.

PS-TuP4 Stabilizing Plasma and RF Generator Interactions*, V. Brouk*, *R. Heckman,* Advanced Energy Industries, Inc.

Current trends towards reduced semiconductor feature sizes has pushed many etch processes into lower pressure regimes, which challenges both stable and accurate RF power delivery at relatively low output power levels. Variations in plasma impedance are more pronounced at lower output powers as compared with operation at higher power levels. In low pressure plasmas that process electronegative gases, operation at low RF output power can result in plasma instabilities that may be attributed to the dynamic interaction between the power-dependent plasma impedance and load-dependent RF delivery system. The power supply and match network control circuits are often unable to counteract these instabilities, sometime even exasperating the problem, resulting in uncontrollable and unrepeatable variations in process parameters. In this study, we will investigate the electrical model that describes how the plasma processing system and the RF delivery system can interact to influence the stability of the plasma. A means for quantifying and measuring the combined stability factor for the RF delivery system and plasma will be shown. This study will review the differences between slow and fast instabilities, and discuss both active and passive stabilization techniques that can increase the stability region for the RF generator and plasma system.

PS-TuP5 Effect of Magnetic Field on the Characteristics of Internal Linear-type Inductively Coupled Plasma Source*, G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea*; K.N. Kim, S.J. Jeong,* Sungkyunkwan University, South Korea

Due to the increase of substrate size and the requirement of high rate processing, large-area high density plasma sources are required for both microelectronics and flat panel display industry. 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 source can not be easily applied to the flat panel display processing due to the standing wave effect, increased capacitive coupling, etc. In our study, a large area (1020mm x 830mm) internal linear inductively plasma source was investigated as a possible high density plasma source for the application to flat panel display processing. Especially, in this presentation, the effect of permanent magnet array on the large area (1020mm x 830mm) linear internal inductively coupled plasma source will be discussed. By the various arrangements of the permanent magnet arrays relative to the inductive source, the uniformity of the plasma has changed significantly, and, by optimizing the magnet arrangement, the plasma uniformity of 2% could be obtained on the substrate. Also, with the optimized magnet arrangement, the photoresist etch rates showed about 60% higher etch rates compared to those without the magnetic field in 15mTorr O@sub2@ gas.

PS-TuP6 Mass and Optical Spectroscopic Studies of an Inductively Coupled Oxygen Plasma*, P.F. Kurunczi,* *V.M. Donnelly,* University of Houston

Mass spectrometry and optical emission spectroscopy were used to measure atomic O in a high-density, inductively coupled oxygen plasma. The plasma reactor consists of a water cooled quartz tube surrounded by a coil powered at 13.56 MHz. An electromagnet confines the high density plasma to the center of the chamber. The walls of the plasma chamber are coated with aluminum oxide. The quadrupole mass spectrometer was line of sight with the center of the plasma. The plasma species pass through a 2mm dia. orifice in the wall of the reactor and traverse through two differentially pumped chambers. With the plasma chamber at 10 mTorr we obtain a background pressure of 5 x 10@super -9@ Torr in the mass spectrometer. The resulting molecular beam was chopped at 103 Hz. with a tuning fork placed between the last aperture and the entrance to the

ionizer, resulting in a beam to background signal intensity ratio of 30:1. Gated pulse counting in phase with the chopping frequency was used to subtract the background from the beam signal. With the plasma off a strong beam signal was observed at mass 32 and a weak signal at mass 16 due the small amount of dissociative ionization of O@sub 2@ at the mass spectrometer ionization energy of 23 eV. With the plasma on the signal at mass 16 increases dramatically due to the formation of oxygen atoms in the plasma. From the known cross sections of O and O@sub 2@ we computed the absolute O atom densities with the plasma on. O atom densities increase proportionally with power and inversely with pressure, reaching 6.5% of the total density at 500 W and 2 mTorr. At 8mTorr and 500 W the percent O dropped to 2.5%. The inverse pressure dependence is ascribed to an increase in electron temperature and resulting increase in the dissociation rate constant. Optical emission actinometry measurements from the center and in directly in front of the mass spectrometer sampling orifice will also be reported and compared with the mass spectroscopic results. Work supported by the Petroleum Research Fund.

PS-TuP7 Sub Millimeter Absorption Spectroscopy of Oxygen Containing Fluorocarbon Etching Plasmas*, **E.C. Benck**, K. Siegrist,* NIST

The role of oxygen in fluorocarbon etching plasmas is investigated using sub millimeter wavelength absorption spectroscopy. The plasmas were created in a specially modified capacitively coupled Gaseous Electronics Conference (GEC) Reference Reactor with a commercial electrostatic chuck. Photoresist and SiO@sub 2@ blanket coated wafers were etched in C@sub 4@F@sub 8@/O@sub 2@/Ar, C@sub 5@F@sub 8@/O@sub 2@/Ar, and C@sub 4@F@sub 6@/O@sub 2@/Ar discharges. The absolute density of various radicals (CF, CF@sub 2@, CHF@sub 3@, COF@sub 2@, CO, etc.) were measured as a function of the percentage of oxygen in the feed gas mixture using a sub millimeter source based on a 48x frequency multiplication chain. These results are also compared to the oxygen containing fluorocarbon gas C@sub 4@F@sub 8@O.

PS-TuP8 In Situ Diagnostics in a High Density Inductively Coupled Methane Discharge*, **T. Meziani**, P. Colpo,* Joint Research Centre of the European Commission, Italy*; P.R. Ranson,* GREMI - Orleans University, France*; F. Rossi,* Joint Research Centre of the European Commission, Italy

The high plasma density, independent control of the ion energy, and low-pressure operation of the inductively coupled plasma source made it very successful for dry etching processes. However, its wide operating pressure range makes it also a tool of interest for PECVD. In this work, a novel inductively coupled plasma source was used for the chemical vapour deposition of diamondlike carbon coatings from a methane precursor. This source uses a special arrangement where the coil antenna is embedded in a magnetic core thus offering high efficiency, high plasma density and very good uniformity. This paper presents the plasma diagnostic of the methane discharge carried out by means of Langmuir probe, mass spectrometry including ion energy distribution measurements, and optical emission spectroscopy. Langmuir probe measurements could be successfully applied taking care of removing systematically the insulating carbon layer formed on the probe tip. The plasma density, electron temperature, and eedf were measured varying different process parameters like inductive power, total pressure, residence time, and gas mixture. Different features were found with EEDF ranging from Maxwellian to Druyvestein or to a bi-temperature distribution at lower pressures. Coupled with mass spectrometry, the probe measurements allowed for the estimation of the absolute mass-resolved ion fluxes impinging on the substrate. The ion energy distributions (IED) were also determined and gave some insight on the formation of the different ions bombarding the growing carbon layer. Mass spectrometry measurements showed that CH@sub 4@ is almost totally dissociated in this source when working with flow rates around 40 sccm at 20 mtorr. Finally, relative radical concentrations were assessed by mass spectrometry and optical emission spectroscopy. The diagnostics results were correlated to the analysis of the carbon coatings and helped explaining the growing mechanisms in our reactor.

PS-TuP9 Electron Probe Currents in ICPs*, **F.F. Chen**,* UCLA

Measurements of plasma density and electron temperature with Langmuir probes in low-density RF plasmas depend on proper compensation for oscillating potentials, but there are further difficulties. In regimes where Orbital-Motion-Limited (OML) theory should be valid, we find that the electron saturation current (Ie) cannot be obtained; instead, Ie rises almost linearly with probe voltage Vp. By monitoring the floating potential with a second probe, we find that a positive Vp on a cylindrical probe greatly affects the space potential Vs, dragging it up with Vp so that saturation is never obtained. This occurs even in a grounded chamber and is characteristic of all electrodeless discharges. The reason is that a large Ie to the probe has to be balanced by an equal ion current to the walls. To increase this ion current, an ambipolar potential has to be set up to push the ions outward against charge-exchange collisions. The drift in Vs to the new equilibrium state can take from milliseconds to seconds. Thus, a DC measurement gives erroneous results and must be corrected by the change in Vs. Another effect is an enhancement of the ion current at large negative Vp. This is probably due to the effect of ion-neutral collisions on the orbiting. Suggestions for improved probe techniques will be presented.

PS-TuP10 Spatio-temporal Characterization of Pulsed, Electron Beam Generated Plasmas for Materials Processing*, **S.G. Walton**, D. Leonhardt,* Naval Research Laboratory*; C. Muratore,* ASEE Postdoctoral Fellow*; R.F. Fernsler,* Naval Research Laboratory

In plasma-based materials modification, regulating the flux of ion, neutral, and radical species at the substrate surface is a critical component of process control. The plasma density determines the flux while the electron temperature influences the energy of these species and so both can be used to regulate reactive species at the substrate. To this end, both modulated plasma production and remote plasma sources are typically employed to control the relative ion and radical fluxes and energy through temporal or spatial variations in the bulk plasma. In this paper, spatio-temporal characterizations of pulsed, electron beam-generated plasmas produced in molecular gases will be presented. Mass and time-resolved measurements of ion fluxes and energy distributions are presented and correlated to measurements of the plasma density, potential, and electron temperature. Previous work has shown that energetic electron beams are efficient at producing high-density plasmas (n@sube@ > 10@super11@ cm@super-3@) with low electron temperatures (T@sube@ < 0.5 eV) over the volume of the beam. The resulting species fluxes and ion energy distributions at remotely located electrodes have unique characteristics and can be useful in range of processing applications. Namely, low ion energies (< 4 eV), regimes of large atomic-to-molecular ion ratio (>1), and ion-to-radical fluxes that are adjustable with electrode position. Modulating the electron beam can further enhance these attributes. Measurements are presented for a range of operating conditions and electron beam-to-electrode distances for plasmas produced in nitrogen, oxygen, TEOS and mixtures thereof. The results compliment and are used to understand various processing applications under development in our laboratory. This work supported by the Office of Naval Research.

PS-TuP11 Study on Relation Between CF2 Radicals and Plasma Parameters in ICP Plasmas with Laser-Induced Fluorescence and Wave Cutoff Probe*, **J.-H. Kim**, Y.-S. Yoo, Y.-H. Shin, K. Chung,* Korea Research Institute of Standards and Science, Korea

The behavior of CF2 radical was studied in CF4 inductively coupled plasma. CF2 radical was measured using a laser-induced fluorescence method [1,2]. Absolute electron density was measured using a cutoff probe [3], which was newly developed, and the electron temperature was measured using a double probe to study relation between the electron property and CF2 radical. CF2 density is drastically changed by variations of operating pressure, ratio of mixed gases and RF source power. To examine the relation between electron density and CF2 radical, CF2 radical and electron density were measured as varying the RF power which is a major external parameter influencing to the electron density. As the RF power was increased, CF2 radical density increased in the range of low electron density and then decreased over a critical electron density. Dependence of CF2 radical density on the electron density was theoretically analyzed with rate equations. The theoretically analyzed relation between the electron density and the CF2 radical density was in good agreement with the experimental result. @FootnoteText@ [1] G. Cunge, P. Chabert and J.P. Booth, J. Appl. Phys. V89, p7750 (2001). [2] S. Hayashi, K. Kawashima, M. Ozawa, H. Tsuboi, T. Tatsumi, and M. Sekime, Sci. and Tech. Adv. Mat. V2, p555 (2001). [3] J.H.Kim, D.J.Seong, J.Y.Lim, and K.H.Chung, Appl. Phys. Lett. V83, p4725 (2003).

PS-TuP12 Simulation Study of Plasma Display Panel Micro Discharge at Atmospheric Pressure Regime*, **S. Mukherjee**, J.K. Lee,* Pohang University of Science and Technology, South Korea, S. Korea

Plasma display panels (PDPs) are high pressure micro discharges that are promising sources of light, ions and radicals. The cell dimensions in a conventional PDP are in the order of microns and operated at high pressures of 400-500 Torr. In our study we operate the panel at pressures in atmospheric range to study the distinction in the characteristics of the discharge. At constant pd value of 10 Torr-cm by increasing pressure p (ranging from 0.5 to 2 atm) and reducing gap length d (up to 60 microns),

we observe similar discharge characteristics as of conventional PDP. The Xe concentration is varied from 10 to 50 percent under such pressures in the Ne-Xe gas mixture that is used in our simulation, to observe the predictable increase in the driving voltage and anomalous behavior of the emission spectra at the dielectric at such pressures and concentrations. It is also beneficial to the study the variation in efficiency, power consumption, density of electrons and metastables at such pressures and concentrations. The UV emission line spectra for excited Xe (3P1) are also affected at such high pressures. We also investigate the difference in the discharge characteristics in the presence and absence of radiation trapping@footnote 1@ and dimers@footnote 2@ in our fluid simulation. @FootnoteText@ @footnote 1@H.C. Kim, S.S. Yang, and J.K. Lee, J. Appl. Phys. 93(12), 9516 (2003).@footnote 2@K. Wojciechowski et.al, Radiation Physics and Chemistry 99, 85(6).

PS-TuP13 Effects of a Pulse Duty Ratio in Dual Frequency Capacitively Coupled Plasma and a Magnetic Field by a Three-Dimensional Charge-Up Simulation*, **S.J. Kim**, S.J. Wang,* Pohang University of Science and Technology, South Korea*; H.J. Lee,* Pusan National University, South Korea*; J.K. Lee,* Pohang University of Science and Technology, South Korea, S. Korea

A dual frequency Capacitively Coupled Plasma (CCP) which independently controls an ion flux and an ion energy is widely used for typical dielectric etching. However, it induces a charge-up damage, which has a harmful effect on the reliability of a device. We have studied charge-up effects in the dual-freq. CCP by a three-dimensional charge-up simulator. In the charge-up simulator [1], the Laplace equation for an electric field calculation is solved. The energy and the angle distributions of ions and electrons used as input parameters are obtained in the dual-frequency CCP by a one-dimensional Monte-Carlo Particle-in-Cell (PIC) simulation [2]. In the dual-frequency CCP, 2MHz pulse is used as a low frequency source and a high frequency is 27MHz. Pulse conditions such as a rising time and a sustain time of the pulse which influence a plasma density and an electron temperature are investigated. The charge-up damage is produced by different motions of ions and electrons. Thus, negative ions as a substitute for electrons reduce the charge-up damage. A pulse duty ratio controls the ratio of a positive ion flux to a negative ion flux in oxygen plasma. Optimal conditions of a pulsed discharge are obtained in order to reduce the charge-up damage and to increase the etch rate. A magnetic field is applied to substrate as a method for the reduction of the charge-up damage. The effect of the magnetic field on the substrate is investigated by the 3D charge-up simulation. This work is supported by the national program for Tera-level nanodevices in Korea Ministry of Science and Technology. [1] H.S. Park, S.J. Kim, Y.Q. Wu, and J.K. Lee, "Effects of plasma chamber pressure on the etching of micro structures in SiO2 with the charging effects", IEEE Trans. Plasma Science 31 (4), 703 (2003). [2] H.C. Kim, J.K. Lee, and J.W. Shon, â?oDischarge asymmetry induced by the pulse radio-frequency currentâ?• , Appl. Phys. Letts. 84, 864 (2004).

PS-TuP14 Time and Space Resolved Optical Emission Spectrogram of Inductively Coupled Chlorine Plasmas for Etch Process*, P.H. Huang,* ***T.L. Lin,*** National Tsing Hua University, Taiwan*; K.C. Leou,* National Tsing Hua University, Taiwan, ROC*; H.J. Ding, C. Lin,* National Tsing Hua University, Taiwan

The applications of optical emission spectroscopy as a quantitative plasma diagnostic technique are powerful tools with the highest benefit being noninvasive measurements of chemically complex discharges. The major task of this work@footnote 1@ was to develop a time and space resolved spectrograph measurement systems of plasma induced emissions from processing plasmas, such as plasma etchers. We used the optical emission tomography (OET) technology and optical emission actinometry (OEA) principles to measure Cl@super +@, Cl and Cl@sub 2@ density variations with space and time in a high density inductively coupled plasma (ICP). The measurement system consisted of a 3 channels spectometer and a motor driven scanning stage mounted on a slot shaped vacuum window on the processing chamber. The optical emissions were sampled by a optical fiber adaptor mounted on the motorized stage which can scan across the chamber horizontally. Due to the configuration of the scanning system, the sampled optical emissions from the plasma are not at the same point in the space-time phase space. A polynomial interpolation method was employed to obtain spectra intensities of Cl@super +@, Cl and Cl@sub 2@ at the same point in space-time phase space. Consequently, we could analyze the spatial-temporal transient behaviors. Experimental results show that spatial profiles of Cl@super +@, Cl, Cl@sub 2@ densities evolve in significantly different trend during the etch process. This might be results from the generation of etch products, SiCl@sub x@, and changing of chamber wall conditions. @FootnoteText@ @footnote 1@ This work has been supported by the National Science Council, ROC, grant no. NSC 92-2218-E-007-019.

PS-TuP15 Controlling of UV Radiation Damages using On-wafer Monitoring Technique*, **M. Okigawa**, Y. Ishikawa, Y. Katoh, S. Samukawa,* Tohoku University, Japan

Gate insulator for metal-insulator silicon (MIS) devices needs high breakdown voltage, low leakage current and low interface states for robust semiconductor devices. Generation of electron-hole pairs in dielectric film as the gate insulator was measured by using our developed on-wafer monitoring technique during the plasma etching processes. To detect the generation of electron-hole pairs by plasma-induced electrical current in the insulator, we developed four types of on-wafer monitoring devices. Each device has an insulator structure such as single SiO@sub 2@ film, single Si@sub 3@N@sub 4@ film, SiO@sub 2@ film stacked on Si@sub 3@N@sub 4@ or Si@sub 3@N@sub 4@ film stacked on SiO@sub 2@. We found that the electron-hole pairs were generated in the insulators by the plasma-induced ultraviolet (UV) photons. We use three gas mixtures (CF@sub 4@+O@sub 2@, C@sub 2@F@sub 4@+O@sub 2@ and C@sub 4@F@sub 8@+O@sub 2@) to vary the wavelength of the emitted UV light in the plasma. The induced current depended on the UV wavelength meaning gas chemistry and the on-wafer monitoring device structures. In the SiO@sub 2@ film, CF@sub 4@ induced the most current of the three gas mixtures because CF@sub 4@ emitted the strongest intensity of the UV light having shorter wavelength than 140 nm as the SiO@sub 2@ band gap of 8.8eV. On the other hand, in the case of the Si@sub 3@N@sub 4@ single film, C@sub 4@F@sub 8@ has larger plasma induced current than other two gas mixtures. C@SUB 4@F@sub 8@ has the most intense UV lights of shorter than 250 nm that is the band gap of Si@sub 3@N@sub 4@, 5.0eV. Additionally, we evaluated the plasma-induced current using multi-layer insulator devices that consisted of both SiO@sub 2@ and Si@sub 3@N@sub 4@. The structure of Si@sub 3@N@sub 4@ on SiO@sub 2@ drastically reduced the plasma-induced current as compare with the structure of SiO@sub 2@ on Si@sub 3@N@sub 4@. This might be caused by the difference of the band-energy structure between them.

PS-TuP16 Diagnostic Studies on a H@sub 2@-N@sub 2@ Inductively Coupled Plasma for Plasma-Assisted Atomic Layer Deposition*, **S.B.S. Heil**,* Eindhoven University of Technology, The Netherlands, Netherlands*; E. Langereis, R. Engeln, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

A new reactor has been constructed for plasma-assisted atomic layer deposition (PA-ALD) of single-element metals and metal nitrides. Besides a vapor dosing system, the reactor consists of an inductively coupled plasma in which H, N, and NH@sub x@ radical species can be produced by operating the plasma on H@sub 2@, N@sub 2@, or NH@sub 3@ and mixtures of these gases. These radicals and possibly other activated neutrals can be used for abstraction of ligands from adsorbed metal halide precursor gases such that also non-binary materials can be deposited by ALD. We have investigated H@sub 2@ and N@sub 2@-H@sub 2@ plasmas by double Langmuir probe measurements and by optical emission spectroscopy. These measurements have been carried out for different plasma conditions and flow ratios while the OES data have been taken at different spatial positions. With OES we have observed the different atomic hydrogen lines as well as the H@sub 2@ Fulcher bands and the first and second positive systems of N@sub 2@. With the Langmuir probe measurements typical electron and ion densities of ~10@super 10@ cm@super -3@ and electron temperatures within the range of 2.5-3 eV have been obtained in the downstream region of the plasma. Currently, the first PA-ALD experiments of Ti and TiN films (e.g., for Cu diffusion barriers) are being carried out using the combination of TiCl@sub 4@ and H@sub 2@(-N@sub 2@) plasmas. The resulting film properties obtained under the different operating conditions will be compared with the results from the plasma studies.

PS-TuP17 Estimation of the Surface Potential Generated on Semiconductor Dielectric Materials Upon Exposure to Vacuum Ultraviolet Radiation Using a Monte-Carlo Simulation@footnote 1@*, **G.S. Upadhyaya**, J.L. Shohet, J.L. Lauer,* University of Wisconsin-Madison

The effect of Vacuum Ultraviolet Radiation (VUV) on dielectric materials during plasma processing is significant. During processing, charge deposited on the material due to the plasma can adversely affect device reliability. Plasma-generated VUV radiation can beneficially deplete the charge by temporarily increasing the conductivity of the dielectric.@footnote 2@ This effect has been attributed to photoemission

and photoconduction currents generated by VUV exposure.@footnote 3@ This can result in a positive surface charge, which is measured using a Kelvin Probe. However, the transport of electrons and holes generated by VUV radiation inside the dielectric is not well understood. To this end, we utilize a Monte-Carlo code, which includes the different processes that an electron undergoes once it has been released from an atom by a VUV photon. The code includes Rayleigh scattering of the incident VUV photons inside the dielectric, photoelectric absorption, and elastic and inelastic scattering of photoemitted electrons. The statistical data obtained from the simulation, such as the backscattering percentage for the electrons, the absorption coefficient of the electrons inside the dielectric, and the distances traveled by the electrons and holes is used to compute the surface potential generated on the dielectric. The simulation estimate is found to be in very good agreement with the experimental measurements made using the Kelvin Probe technique. The cross sections used for the various processes in the VUV regime are based on previous work where available. The remaining cross sections are estimated from experimental measurements in which synchrotron radiation is incident on the dielectric. @FootnoteText@ @footnote 1@ Supported by NSF under grant DMR-0306582. The UW Synchrotron is funded by NSF under grant DMR-0084402.@footnote 2@ C. Cismaru and J.L. Shohet, Appl. Phys. Lett. 76, 2191 (2000)@footnote 3@ J.L. Lauer, J.L. Shohet, et. al., J. Appl. Phys. 91, 1242 (2002).

PS-TuP18 Induced Charge during Vacuum-Ultraviolet Irradiation of Al@sub 2@O@sub 3@, SiO@sub 2@, and Si@sub 3@N@sub 4@@footnote 1@*, J.L. Shohet, J.L. Lauer, R.W. Hansen, G.S. Upadhyaya, R.D. Bathke, K. Kukkady, J.M. Kalwitz,* University of Wisconsin-Madison

Plasma damage, contamination, and thermal budget are key concerns in the microelectronics industry. In particular, dielectric charging plays a key role in processing damage of semiconductor devices. During the last decade, plasma-induced damage research has mainly focused on the role of charged particles in the plasma with little or no consideration being given to photon bombardment. VUV radiation with energies in the range of 4-30 eV can induce charge on electronic materials. Radiation charging of Si wafers coated with 3000A of Al@sub 2@O@sub 3@, SiO@sub 2@, and Si@sub 3@N@sub 4@ from synchrotron VUV exposure with photon fluxes in the range of 10@super 9@-10@super 13@ photons/sec cm@super -2@ was measured. The total charge induced on the dielectrics during VUV exposure, which can be measured with a Kelvin Probe, consists of charge due to photoemission and electron-hole pair creation. The photoemission current and substrate voltage were monitored during each exposure for various bias voltages. For photon energies of 7-21 eV, the integral of photoemission current was compared to the net charge measured with the Kelvin probe which allows us to separate the charging affects of photoemission from that of electron-hole pair creation within the dielectric. Since the threshold photon energy for photoemission is higher than that for electron-hole pair production, it is seen that photoemission can be minimized if the photon energies are below the threshold energy. This produced the possibility to reduce dielectric charging, especially that induced by electron-shading effects during plasma etching of high aspect-ratio devices, by providing a safe way to discharge these structures and, thus, minimize plasma-charging damage. The enhanced conductivity may benefit etching properties such as reduction of notching, sidewall bowing, and trenching. @FootnoteText@ @footnote 1@This work is supported by NSF under grant DMR-0306582. The UW Synchrotron workis funded by NSF under grant DMR-0084402.

PS-TuP19 Electrical Characteristics of Linear Internal-type Inductively Coupled Plasmas Source*, G.Y. Yeom,* Sungkyunkwan University, South Korea, Korea*; **K.N. Kim**, S.J. Jeong,* Sungkyunkwan University, South Korea

Inductively coupled plasma ICP sources have been studied extensively in the past ten years as candidates for advanced etch and deposition processing tools. Although ICP plasma sources have many advantages, the plasma generated is inherently non-uniform due to the antenna standing wave effect, when the plasma source is scaled to large size comparable to the driving rf wavelength. In this study, large-area plasmas with inductive coupling of extended internal linear- antennas have been proposed a promising candidate for an efficient high-density plasma source. The process chamber was designed as a rectangular mainly for 4th generation FPD application and was made of stainless steel. The inner size of the chamber was 1020mm*830mm. The characteristics of the plasmas were measured using a quadrupole mass spectrometer and a Langmuir probe located on the sidewall of the chamber. And the electrical characteristics of linear antennas were measured using an impedance probe. The results showed a strong relationship between the antenna design and plasma characteristics such as density and uniformity. Under an optimized antenna design, the uniformity of the Ar@super+@ ion density less than 4% could be obtained while maintaining high plasma densities on the order of 2.67*10@super11@cm@super-3@.

PS-TuP20 Effects of Water Vapor on Plasma Parameters in Processing Plasmas*, **Y. Ichikawa**, M. Narita, K. Sasaki,* Fuji Electric Device Technology Co., Ltd., Japan

We have studied the effects of a trace amount of water vapor on the properties of processing plasmas by numerical analysis. In plasma processing for semiconductor applications such as sputtering and plasma CVD, oxygen is easily incorporated in the deposited films or in the ambience of plasma and seriously influences the properties of films and the performance of semiconductor devices. The principal source of oxygen is water vapor emitted from the wall of reaction chambers. Thus it is very important to understand the behavior of water vapor in processing plasmas. With a view to understanding the effect of water vapor on the processing plasma, we made a modeling of Ar positive column plasma; Ar is most popularly used for plasma processing in all the rare gases. The analytical method employed here is based on a positive column theory of Ichikawa and Teii.@footnote 1@ In the modeling, we took into account 6 ion species, Ar@super +@, Ar@sub 2@@super +@, H@sub 2@O@super +@, H@sub 3@O@super +@, OH@super +@, H@super +@ and meta-stable Ar. The reaction scheme among these species is very complicated, but assuming a small amount of H@sub 2@O in Ar, we can simplify the reaction system. The obtained results show that the abundance ratios of H@sub 2@O@super +@ and H@sub 3@O@super +@ become comparable to that of Ar+ even if a very small amount of H@sub 2@O, e.g. less than 1%, is added in Ar; these H@sub 2@O related ions increase with increasing gas pressure and chamber size. We will present the details of ion-molecule reactions used in the modeling for the Ar-H@sub 2@O plasma and numerical results. @FootnoteText@ @footnote 1@Y. Ichikawa and S.Teii, J. Phys. D, 13, 2031 (1980).

PS-TuP21 Evaluation of Germicidal Effect by Plasma Sterilization System in Air*, **J.H. Choi**, H.K. Baik, J.C. Park, D.W. Han,* Yonsei University, Korea

Atmospheric pressure(AP) plasmas can sterilize almost all kinds of bacteria because many germicidal species, such as atomic oxygen, hydroxyl radical and ozone etc. are generated during AP plasmas. So AP plasmas are proper process for application to air cleaner or sterilizer. The aim of this paper is to evaluate a germicidal effect by plasma sterilization system in air. For this experiment, we modified the inhalation exposure system used for experiment to infect animal. By the nebulizer in our plasma sterilization system, aerosol attached to bacteria in culture media was generated, and therefore we could make a proper process to evaluate the germicidal effect of air cleaner including AP plasma system. We made 3 types of plasma reactor and these are dielectric barrier discharge, surface barrier discharge and pack-bed discharge type. We used alumina and copper for dielectric and electrode material respectively. And in many sorts of bacteria, e-coli, pseudomonas aeruginosa and bacillus subtillus were used for this sterilization experiment. For analysis of the relationship between sterilization results and chemical species generated in discharge, we used optical emission spectroscopy (OES) and we checked emission spectra by atomic oxygen (394.2nm and 436.8nm) and O2+ ion (631.4nm). From these results, we concluded that our AP system is very effective to evaluate germicidal effect.

PS-TuP22 Extending the "Winters and Coburn Method"@super 1@ to Plasma Propellant Interactions*, **R. Valliere**, R. Blumenthal,* Auburn University

There has been a significant interest in the use of plasmas to ignite propellants, specifically for large bore artillery. A short, reproducible ignition delay and a reduced temperature dependence are the most important advantages of plasma ignition over conventional ignition. The fundamental interactions of plasma and the propellant have been investigated using the experimental modeling method, pioneered by Winters and Coburn,@super 1@ that is responsible for our current understanding of the etching of semiconductors. The erosion rates of sprayed-on films of RDX and HMX have been measured in inert and reactive plasmas, with both negative and positive sample biases in order to select ion and electron bombardments of the propellant surface. No significant erosion rate was observed in argon plasmas with zero or any positive applied bias, indicating that erosion by electron bombardment alone is not important. Under large negative bias, ion bombardment conditions, a small erosion rate was observed. The minimum of erosion rate found for all positive and zero sample biases in hydrogen plasmas was

100x the erosion rate of the negatively-biased argon plasmas. Above a threshold of approximately -250V DC bias, the erosion rate in the hydrogen plasmas increases by another order of magnitude. The fact that the etch rates in the hydrogen plasmas are all much greater than the sputter rate of the argon plasmas (observed at large negative bias) indicates that the process in hydrogen plasmas is chemically enhanced and has strong synergistic effects. Detailed results of the individual roles and synergistic interactions of ions, H radicals and electrons with the propellant surface will be presented. @FootnoteText@ @footnote 1@H.F. Winters and J.W. Coburn, J. Vac. Sci. Technol, B 3(5), 1376 (1985).

PS-TuP25 The Fate of Nitrogen in Plasma Polymerization Revealed by NEXAFS*, **A.G. Shard**, S.L. McArthur,* University of Sheffield, UK*; J.D. Whittle,* Plasso Technology, UK*; A.J. Beck, R.A. Talib,* University of Sheffield, UK*; N.A. Bullett,* University of Sheffield, UK, United Kingdom*; P.N. Brookes,* University of Sheffield, UK

The determination of plasma polymer chemistry is often rather difficult due to the large numbers of candidate functional groups. Conventional analytical methods such as X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy have limitations, particularly with regard to nitrogen containing plasma polymers. In these polymers there are potentially a number of functional groups which cannot be distinguished from amines by XPS such as aromatic amines, pyridinic structures, imines and nitriles. With IR spectroscopy there are also difficulties in identifying some of these species, coupled to a lack of quantification. The presence of such groups may impair the effectiveness of plasma polymerized amines in their ability to interact electrostatically and to be available for imine coupling reactions so their detection is a matter of some importance. Near edge X-ray absorption fine structure (NEXAFS) can easily distinguish the presence of the unsaturated species mentioned above. We have applied this technique to a range of nitrogen containing plasma polymers and show that the ultimate fate of nitrogen, particularly at high powers, is to produce nitrile groups. We have studied saturated and unsaturated amine and amide containing monomers and a copolymerisation of allylamine and acrylic acid. This study has implications for potential new uses of such materials and indicates that the long term oxygen incorporation into aminated plasma polymers may be due to hydrolysis of imine and nitrile groups.

Plasma Science and Technology
Room 213A - Session PS1-WeM

Plasma in Nanoscale Applications

Moderator: W.M. Holber, MKS Instruments

8:40am **PS1-WeM2 Growth, Characterization and Application of Plasma-Assisted Nano-Coatings***, **P.P. Joshi**, R.V. Pulikollu, S. Higgins, S.M. Mukhopadhyay,* Wright State University

Plasma-assisted coatings have significant application potential as they can be tailored to impart desired properties to the surface. The goal here is to develop a fundamental understanding of the initial stages of growth of these coatings on model flat substrates, and then test the applicability of these on uneven structures. Two types of plasma assisted functional coatings are studied: viz. oxide coatings that imparting surface reactivity (or hydrophilicity) and fluorocarbon coatings that imparting surface inertness (or hydrophobicity). XPS was used for detailed study of chemical composition of the substrate and coating atoms at various stages of deposition. Atomic force microscopy was used to study the morphology of these coatings as they grow. Combined XPS and AFM results for both the coatings rule out any possibility of the patchy coatings with exposed substrate (complete coverage of substrate), and also indicate that these coatings are effective on nanometer scale. These studies show that plasma-assisted chemical deposition can be a very viable approach to creating functional nano-coatings on surfaces of nano-structured solids. Initial studies on single-crystal silicon were followed up with comparative studies on different types of substrates (sapphire, graphite etc.). The effectiveness of these coatings on uneven surfaces such as composite core structures and fibrous films will be discussed.

9:00am **PS1-WeM3 Plasmas Technologies in Microfluidics for Novel Bioanalytical Systems***, **T. Ichiki,*** Toyo University, Japan **INVITED**

Development of innovative nano-bio-analytical systems is coming to reality by the combination of the microfluidic device technologies and the precise image processing systems using an optical microscope or a scanning probe microscope. Highly functional microfluidic devices can be fabricated by the application of advanced nano/microfabrication technologies developed in the ULSI industry. Microfluidic devices under development in our projects are expected to enable direct manipulation and analysis of each single cell and obtain molecular-level information about life phenomena of the cell, which has not been attainable by the conventional analysis tools. Recent progress and the future scope in plasma processing for microfluidic devices will be presented in this paper.

9:40am **PS1-WeM5 Fabrication of 7nm High Aspect Ratio Nanocolumns by Low Energy Neutral Beam Etching using Ferritin Iron-Core Mask***, **T. Baba**, T. Kubota,* Tohoku University, Japan*; Y. Uraoka, T. Fuyuki,* Nara Institute of Science and Technology, Japan*; I. Yamashita,* Matsushita Electric Industrial Co., Ltd., Japan*; S. Samukawa,* Tohoku University, Japan

The critical dimension of semiconductor devices is continuously expected to be decreased up to less than 50 nm within the next decade. However, the conventional lithography has a theoretical limit to define patterns smaller than wavelength of light. In this study, we report a new method to fabricate nanometer-scale structure by using biomaterial etching mask and a newly developed neutral beam etcher. A large number of atomically equal molecules can be easily produced due to the nature of biomaterials, such as proteins, that are synthesized based on the DNA information. Ferritin is a type of proteins, which is capable of biomineralization to make inorganic materials. It can biomineralize iron-core as hydrated iron oxide. By using the iron-core as an etching mask, we fabricated a number of 7nm nanocolumns in their diameters. Neutral beam etcher has been employed in this experiment. Neutral beams could realize accurate and damage-free etching because it could prevent charged particles and ultraviolet photons. Employing the uniform iron-core mask and neutral beam etching, high aspect ratio nanocolumn structure was successfully fabricated, and almost vertical sidewalls profiles were able to be achieved. The aspect ratio of 6.57 was achieved with 7 nm of the diameter, which was identical to that of the iron core. The neutral beam enabled damage-free etching and led to an accurate transfer from the iron-core to the silicon substrate without any aggregation of the iron-cores.

10:00am **PS1-WeM6 Deposition of Nanocomposite Layers for Ultralow Dielectric Applications***, **G.R. Alcott**,* TNO-TPD, The Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; J. Linden,* TNO-TPD, The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

As the dimensions of integrated circuit devices scale to smaller feature sizes, the resistance-capacitance (RC) delay of the metal interconnect will increasingly limit the performance of high speed logic chips. The integration of ultralow dielectric materials ($k < 2.5$) can reduce this problem and the use of the porous materials is now deemed necessary if the future targets of chip design are to be achieved [@footnote1@]. While many candidates for ultralow-k applications exist, many of the most promising are synthesized using wet chemical processes involving harmful solvents and multiple process steps. In this work a novel dual plasma reactor is used to simultaneously synthesize and incorporate porous nanometre sized particles into SiO@x@C@y@H@z@ layers. Porous nanoparticles and siloxane layers are synthesized from a TEOS/O@2@ and 1,2-bis(trimethyl)siloxyethane precursors respectively. Structure and composition of the nanocomposite layer produced are characterised using ESEM and infrared absorption spectroscopy. Thermal stability and electrical properties are determined to evaluate the thin films suitability in low-k dielectric applications. Dielectric constants as low as 1.82 ± 0.02 were achieved at 1 MHz. @FootnoteText@ @footnote1@ http://public.itrs.net.

10:20am **PS1-WeM7 Nano-Scale Pattern Transferring By Plasma Etching***, **Y. Zhang**, C. Black, K. Guarini, T.J. Dalton,* IBM T. J. Watson Research Center **INVITED**

Patterning challenges for the 22nm node and beyond in the ITRS roadmap requires precision etching of semiconductor nano-scale features at the sub-10nm regime. In this paper, we report the recent results of patterning true nano-scale features using plasma etching. A newly established method called "nanometer-scale pattern registration and alignment by directed diblock copolymer self assembly" was employed. Using this technique, large-scale (across 200 mm wafers) high-density (> 10E6/cm2) nano-scale features were produced; both holes and line arrays with 40nm pitch were fabricated. These structures are beyond any state-of-art conventional optical lithography and e-beam writing technologies. The nanometer holes & line arrays were used to study plasma etching characteristics and challenges for different materials (silicon, silicon dioxide, and silicon nitride) with different plasma chemistries (fluorine-, chlorine-, and bromine-based). Besides scaling of the feature size or critical dimension, the thickness of the film stacks to be etched were also scaled. The patterning of nano-scale line arrays was more challenging that the patterning of nano-scale hole arrays when using ultra-thin and ultra-narrow diblock polymer masks. Among the challenges for line arrays were: (1) deformation of the polymer masks (due to poor thermal conductivity and film stress); (2) depth limitations due to selectivity to the mask; and (3) line edge roughness, (LER). These challenges have not only made the pattern transferring more difficult (even with current state-of-art plasma etching tools), but also indicate that plasma etching may be approaching a limits as it is currently implemented. A few proposed limiting factors of current etching tooling, underlying principles of different chemistries, and processing parameters and their advantage and drawback to etching nanometer scale features will also be discussed.

11:00am **PS1-WeM9 Crucial Role of Side Wall Deposition during Synthesis of Spatially Separated Vertically Aligned Carbon Nanofibers by C-PECVD***, **A.V. Melechko**,* University of Tennessee, Knoxville*; D.K. Hensley,* Oak Ridge National Laboratory*; X. Yang, K.L. Klein,* University of Tennessee, Knoxville*; H.M. Meyer, D.H. Lowndes,* Oak Ridge National Laboratory*; M.L. Simpson,* Oak Ridge National Laboratory, University of Tennessee

Catalytic plasma enhanced chemical vapor deposition (C-PECVD) is used for deterministic synthesis of vertically aligned carbon nanofibers(VACNFs). In this process the location, orientation, diameter and length of the fiber can be controlled. Deterministic synthesis is extremely important for incorporation of nanofibers into devices with nanoscale elements such as microfabricated electron field emission sources, gene delivery arrays, intracellular electrochemical probes, scanning probe microscopy tips etc. In C-PECVD the formation of the carbon nanofiber via the catalytic particle is accompanied by the non-catalytic deposition of an amorphous carbon film over the surface. In order to prevent the undesirable film formation carbon source gas is diluted with etchant gases and the reactor is operated in an etching rather than deposition regime. The operating parameters usually are tuned so that the removal rate of carbon film is exactly equal to its deposition rate so that the growing nanofiber is not damaged. This is

especially important for isolated nanofibers as their sidewalls are completely exposed. Such a balance is difficult to maintain over large-scale substrates with non-uniform patterns. We will report on a new regime in which Si from the substrate participates in the formation of a protective coating on the nanofiber sidewalls. In this process the formation of a carbon film is completely eliminated and the functionality of the VACNF is not affected. The results of SEM, EDX and AES with spatial resolution were used to determine the atomic composition and structure of coated carbon nanofibers. The dependence of side wall deposition on the plasma power, gas flow ratio and pressure will be discussed. In addition, a solution for non-silicon substrates will be offered.

11:20am **PS1-WeM10 Catalytic Plasma Enhanced Chemical Vapor Deposition of Ultrasharp Vertically Aligned Silicon Nanocones and Their Characterization***, **K.L. Klein**, A.V. Melechko,* University of Tennessee/ORNL*; P.D. Rack,* University of Tennessee*; D.K. Hensley,* Oak Ridge National Lab*; J.D. Fowlkes,* University of Tennessee*; H.M. Meyer III, L.F. Allard, D.H. Lowndes,* Oak Ridge National Lab*; M.L. Simpson,* University of Tennessee/ORNL

We present a new method for the synthesis of vertically aligned ultrasharp silicon nanostructures with tip diameters as small as 10 nm. Silicon nanocones were produced using dc plasma-enhanced chemical vapor deposition (dc-PECVD) using the Si substrate as a sole source of Si and thin film Cu or Au as a catalyst. High resolution SEM, TEM, EDX, STEM, and AES were utilized to determine the microstructure and composition of the nanocones. We have explored variations in the structure and growth mode of these nanocones with respect to growth conditions. This structure will be described in detail and a growth mechanism proposed. The similarities and differences of this new growth process as compared to standard SiH4-based VLS growth will be discussed. Finally, we will describe their potential use in applications such as gene delivery arrays and field emission cathodes.

11:40am **PS1-WeM11 Gas-Phase Synthesis of Single-Walled Carbon Nanotubes by Hot-Filament-Assisted Plasma Chemical Vapor Deposition and Its Analysis by Mass Spectroscopy***, **Y. Hayashi**, Y. Morimoto, Y. Kogawara, S. Nishino,* Kyoto Institute of Technology, Japan

Single-Walled Carbon Nanotubes (SWNTs) have been successfully synthesized in gas phase by Hot-Filament-Assisted Plasma Chemical Vapor Deposition. Hot filaments were used for heating a reaction zone and for the assistance of generation and stabilization of DC plasma. Ethylene diluted 30 % in hydrogen was flowed through a pipe into a stainless chamber to the direction of the hot filaments. The vapor of ferrocene was included into the reaction gas before introduction to the chamber. Three tungsten wires were stretched and they were heated 1800-2000 °C. The pressure in the chamber was maintained 3.33 kPa (25 Torr). At 25 mm downstream of gas flow from the hot filaments, a cupper plate was placed perpendicular to the flow. DC voltage of +300 V with the current of 150 mA was applied to the cupper plate with the hot filaments and the chamber grounded. Glow discharge plasma was generated between the hot filaments and the cupper plate for about one hour. Carbon fine particles collected on the plate as well as on another plate put under the plasma on the bottom of the chamber were evaluated by Raman spectroscopy and they were confirmed to be SWNTs. The diameter of the SWNTs were observed by transmission electron microscopy to be 1 to 2 nm. The fact that more SWNTs were obtained on the bottom plate than on the downstream plate suggests their synthesis in gas phase. Quadrupole mass spectrometry was carried out for the analysis of molecules during the synthesis. The evolution of partial pressure of benzene corresponded well with the evaporation of ferrocene while that of iron did not. The results support that iron clusters were formed in gas phase through the decomposition of ferrocene and that large amount of SWNTs were grown on them being suspended in the glow discharge plasma for a long time.

Plasma Science and Technology
Room 213B - Session PS2-WeM

Plasma Sources

Moderator: J. Caughman, Oak Ridge National Laboratory

8:20am **PS2-WeM1 Langmuir Probe Measurements of Change in Plasma Parameters with Change in Chamber Geometry in Electronegative Plasmas***, **S.P. Sant**, E.A. Joseph, B.S. Zhou, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

The affect of chamber geometry on the characteristic behavior of two electronegative gases commonly used in the processing industry, namely CF@sub 4@ and O@sub 2@ were studied. The chamber used is the modified Gaseous Electronics Conference (mGEC) reference cell. The mGEC was designed to allow rapid changes to its geometrical structure and wall materials, allowing us to closely inspect various plasma-wall interactions. A Langmuir probe was used to obtain axial and radial measurements of ion density, electron density, plasma potential, electron temperature and floating potentials. These parameters were measured for a combination of two different source â?" chuck gaps (4 cm and 9.8 cm) and chamber diameters (20 cm and 64 cm). It is observed for both gases, that the electron temperature ranges from ~ 5 eV to ~ 1 eV as we move from the center towards the walls in the 64 cm diameter case with the narrow gap. For wider gap the peak temperatures are ~ 30% lower for O@sub 2@ case only, while they remain approximately the same for CF@sub 4@. In comparison, the plasma density drops by a factor of 2 in the center (1.5 E 11 to 0.8 E 11) with decrease in gap, but the center density remains fairly constant independent of chamber diameter. In general, it is observed that the experimental values vary with change in gap (coil to chuck distance), but remain fairly constant with change in chamber diameter. This work is supported by a grant from NSF/DOE, CTS â?" 0078669.

8:40am **PS2-WeM2 Modeling of a Commercial Dual Frequency Magnetically Enhanced Capacitively Coupled Plasma Reactor with Rotating Static Magnetic Field***, **T. Panagopoulos**,* Applied Materials, Inc.*; A.M. Paterson, J.P. Holland,* Applied Materials Inc.

Magnetically enhanced reactive ion etching (MERIE) reactors have recently been modeled for 200mm wafer processing chambers with single frequency and uniform static magnetic field. An extension of this work is presented for a commercial 300mm dual frequency MERIE reactor with rotating static magnetic field for an argon discharge. The magnetic field is modeled in the 3D space (CFD-ACE) and it is used as an input in a 2D computational model (HPEM). The different moments of the static magnetic field are solved independently and the species spatial profiles are compared for different magnetic field intensities and operating pressures. The use of magnetic field results in more confinement of the ion density within the area of the two electrodes. This confinement is more effective for lower pressures (10s of mTorrs) and tends to confine the plasma at the wafer center. On the other hand, when the pressure increases to a few hundreds of mTorrs, the plasma density is confined close to wafer edge. The density profiles are affected by the time averaged ionization source by bulk electrons. When no magnetic field is applied in the chamber, the ionization source is located near the wafer edge and in the middle of the inter-electrode spacing. As the magnetic field increases in a high pressure regime, the ionization sources move closer to the bottom electrode, and for even higher magnetic field (~100G) most of the ionization takes place at the edge of the bottom electrode with a lessened contribution from the top electrode. For lower operating pressures (~30 mTorr), the ionization patterns are different with a substantial contribution from the top electrode and bulk of the plasma, for average magnetic fields. In a similar way the dc bias is affected by the operating pressure regime; it becomes less negative as the magnetic field increases at low pressures, while it becomes more negative for the high pressure regime. Experimental wafer results agree with the simulation trends.

9:00am **PS2-WeM3 Control of Uniformity in Multifrequency Capacitively Coupled Plasmas Considering Edge Effects@footnote 1@***, **J. Lu**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Multifrequency capacitively coupled plasmas are finding increasing use in etching and deposition applications. The optimization of ion flux uniformity is known to be a sensitive function of the edge electrical boundary condition embodied in the shape, permittivity and conductivity of the guard (or focus) ring. To investigate these geometrical and electrical effects, a 2-dimensional plasma hydrodynamics model has been developed which uses an unstructured numerical mesh. This meshing capability enables fine resolution of the substrate structures. The dependence of the

ion flux uniformity on the electrical boundary condition using single and dual frequency operation (10s MHz and a few MHz with frequencies on one electrode or separate electrodes) will be discussed for process conditions of 10s mTorr in electropositive (Ar) and electronegative (Ar/fluorocarbon, Ar/O@sub 2@) mixtures. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF.

9:20am **PS2-WeM4 Potentials and Fields in a 300-mm Dual-Frequency Capacitively Coupled Plasma Reactor***, **P.A. Miller**, E.V. Barnat, G.A. Hebner,* Sandia National Laboratories*; A.M. Paterson, J.P. Holland, T. Lill,* Applied Materials

Dual-frequency capacitively coupled plasma reactors provide separate control over plasma generation and ion extraction. Usually, a vhf power supply (source) is used to generate and sustain the plasma and an hf power supply (bias) is used to extract ions. At present there is debate over the optimum choices for the two operating frequencies, and whether they should be applied to one or two electrodes. Higher frequencies facilitate plasma generation with mild and controllable dissociation of feed-gas molecules, but the attendant shorter wavelengths cause concern over spatial variations in plasma properties. Regardless of frequency choices, electrical nonlinearity of plasma sheaths causes harmonic generation and mixing of source and bias frequencies. These processes, and the resulting spectrum of frequencies, are as much dependent on electrical characteristics of matching networks as on the plasma sheath properties. We investigated such electrical effects in a 300-mm Applied-Materials plasma reactor. Data were taken for 13.56-MHz bias frequency (chuck) and for source frequencies from 30 to 160 MHz (upper electrode). An rf-magnetic-field probe (B-dot loop) was used to measure the radial variation of fields inside the plasma. We will describe the results of this work. This work was supported by Applied Materials 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.

9:40am **PS2-WeM5 Time and Position Resolved Characterization of ICP and Double-ICP Sources***, **P. Awakowicz,*** Ruhr-Universität Bochum, Germany **INVITED**

Inductively coupled rf sources are important tools in semiconductor plasma processing. In recent years, these tools also have been investigated for medical applications like plasma sterilisation and surface modification of polymers. This is the reason why a double ICP source has been developed. In order to characterize these different plasma sources, Langmuir probe measurements, energy-resolved mass spectrometry, optical emission spectroscopy and plasma modelling have been applied to different ICP sources. For time resolved measurements, Langmuir probe and mass spectrometer were synchronized. Time and position dependent profiles provide a deeper insight into physics of these source and provide additional parameters like puls frequency and duty cycle for adjusting new or improved processes.

10:20am **PS2-WeM7 Comparison of Fluorocarbon Gases and NF3 for Plasma Chamber Cleaning with Transformer-Coupled, Toroidal Source***, **B. Bai**, H.H. Sawin,* Massachusetts Institute of Technology*; L. Gary, M. Mocella,* DuPont Electronic Gases

In recent years, remote chamber cleaning has begun to replace in situ chamber cleaning for Chemical Vapor Deposition (CVD), due to the lower occurrence of chamber wall erosion and lower perfluorocompound (PFC) gas emission. We have tested a high-power transformer-coupled toroidal plasma source typically used with NF3 to produce fluorine atoms for chamber cleaning. The ASTRONex unit couples high power levels (<10 kW) into the feed gases, leading to high neutral temperatures (as high as 6000K) under conditions that produce relatively low electron temperatures. These condition produce very high degrees of dissociation of not only NF3, but also for fluorocarbon compounds â?" contrary to what has been seen in lower power and/or microwave units for remote chamber cleaning. In this work, a systematic comparison has been made among various fluorocarbon compounds (with added O2) including CF4, C2F6, C3F8, and C4F8, along with NF3. Trends in cleaning rates, which are significantly different from earlier studies in other units, will be described. Tool emission studies with Fourier Transformed Infrared Spectroscopy (FTIR), along with analysis of the cleaned surfaces via X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM), will also be presented. Plasma parameters were also measured to better understand the kinetics in the source. Neutral gas temperatures were obtained by fitting rovibrational bands of diatomic species like CO, CF or added N2. Electron temperature and electron density were determined by the atomic argon spectrum, while the atomic concentrations of fluorine and oxygen species in the plasma source were measured by advanced actinometry. For these two optical emission spectroscopy measurements, a full consideration of optical cascading and radiation trapping was necessary due to the high source pressure (~1 torr).

10:40am **PS2-WeM8 Scaling of Low-pressure Ionized Metal PVD Reactors@footnote 1@***, **V. Vyas**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Ionized metal physical vapor deposition (IMPVD) at sub-mTorr pressures is used to deposit diffusion barriers and seed layers onto high aspect ratio trenches. At these pressures, conventional fluid or hybrid simulations are of questionable validity as transport is highly non-equilibrium and a kinetic approach may be warranted. In this work, a Monte Carlo simulation for ion and neutral transport (IMCS) has been developed and integrated into a 2-dimensional plasma equipment model to improve our capabilities to address lower pressures. The ion velocity distributions obtained from the IMCS are used to obtain transport coefficients for use in heavy particle momentum and energy conservation equations, thereby extending their validity to lower pressures. Hollow Cathode Magnetron (HCM) plasma sources for Cu deposition have been investigated using the model while varying power, pressure and source geometry. The consequences of varying these parameters on the uniformity of reactant fluxes, and their energy and angular distributions on the substrate will be reported. Comparisons will be made to experiments for plasma properties and deposition profiles. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF.

11:00am **PS2-WeM9 Production of Meter-scale High-density Microwave Plasmas for Giant Materials Processing***, **H. Sugai**, Y. Nojiri, T. Ishijima, E. Stamate,* Nagoya University, Japan

There has been a great need for meter-scale high-density plasma sources for manufacturing giant microelectronics devices such as liquid crystal display and solar cell. Capacitive discharges at frequencies in VHF range enable us to generate a medium-density meter-size plasma, however standing wave effect and edge effect significantly degrade the plasma uniformity. Here, we present a new technology for production of large-area uniform high-density plasmas based on surface wave excitation at 2.45 GHz. The critical challenges are (1) how to avoid huge atmospheric pressure acting on a dielectric window for microwave radiation, and (2) how to design an antenna-plasma coupling so as to attain the plasma uniformity over meter-size. The first issue is dodged by employment of a dielectric-filled waveguide and slot antennas, which are contained in a low-pressure plasma vessel. The second issue is solved by a careful design of slot antenna and by introduction of corrugated dielectric surface. Surface waves propagating along the interface between a dielectric plate and plasma are investigated in an analytical model and also in FDT simulation. The standing modes of surface waves at 2.45 GHz were successfully detected by a movable antenna, and the mode numbers are in good agreement with the wave theory. In the preliminary experiments using a large discharge vessel (length 1 m, width 0.3 m), we obtained the plasma density of ~5x10@super11@ cm@super-3@ with ~10 % uniformity at 2.5 kW in argon at 50 mTorr.

11:20am **PS2-WeM10 Extraction of a Directional Ion Beam with Controlled Energy Using a Pulsed Plasma***, **L. Xu**, V.M. Donnelly, D.J. Economou,* University of Houston

A 13.56MHz pulsed (typically 50µs ON/50µs OFF), capacitively coupled plasma reactor was developed to generate a nearly monoenergetic, directional ion beam. The DC bias on the target ranged from -150 to -270 volts depending on the input power and pressure. A Langmuir probe was employed to characterize the pulsed Ar plasma and a 3-grid ion energy analyzer was used to measure the ion energy distribution (IED). The EEDF during the power-ON fraction of the cycle was non-Maxwellian with a high energy tail, most likely due to secondary electrons emitted from the target. Beyond 4 µs into the power-OFF period, a Maxwellian EEDF was observed and the electron temperature (T@sub e@) decayed rapidly. The evolution of the EEDF during the power-OFF period was also used to verify the collapse of T@sub e@. After a specified delay in the power-OFF period, a positive voltage pulse was applied to a DC ring electrode surrounding the plasma to raise the plasma potential (V@sub p@) and "push" positive ions through a grounded grid out of the plasma. With the DC ring electrode voltage pulse on, a high-voltage shift of a Langmuir probe IV curve signified an increase of V@sub p@. With 50 V applied to the DC ring, the energy of the extracted ion beam peaked at 49.4 V, while the FWHM of the IED was 4.3 V, limited by the rise time of the homemade voltage pulse circuit. The

ion beam is also expected to be very directional since the ion temperature depends on T@sub e@, which was very low during ion extraction. Finally, the sheath thickness during ion extraction was much larger than the holes of the grid, resulting in a vertical sheath electric field and minimal divergence of the ions as they traversed the grid holes. This was verified by a self-consistent PIC simulation. Work supported by NSF.

11:40am **PS2-WeM11 Particle-in-Cell Simulation of Ion Extraction Through a Grid*, S.K. Nam*,** *V.M. Donnelly, D.J. Economou,* University of Houston

Ion extraction from a plasma through a grid finds applications in ion beam and neutral beam sources. The flux, energy and angular distributions of ions (or neutrals) extracted from the plasma are of primary importance in such applications. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface topography of the extraction grid. For example, when the sheath thickness is comparable to or smaller than the grid hole size, the sheath tends to conform to the surface topography of the grid (plasma molding) resulting in divergent beams. A self-consistent Particle-in-Cell (PIC) simulation of ion extraction from a plasma through a grid was developed. Emphasis was placed on extracting ions, which are as mono-energetic and as directional as possible. The effect of control parameters affecting the sheath thickness (plasma density, electron temperature, sheath potential) relative to the grid hole size (and aspect ratio) was studied. For a hole size of 0.5 mm, the FWHM of the ion angular spread was about 4, 10, and 20 degrees for sheath thickness of 4.3, 2.6, and 0.7 mm, respectively (sheath potential of 50 V, electron temperature 3 eV). Ion flux uniformity was very high for the thick sheath case (within a 3%) but degraded gradually for the thinner sheaths due to stronger ion divergence. Conditions which allowed the extraction of an ion beam with specified energy and angular spread were determined. The influence of hole-hole interaction was also studied. Work supported by the National Science Foundation.

Plasma Science and Technology
Room 213A - Session PS-WeA

Plasma Diagnostics

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

2:00pm **PS-WeA1 Excitation Mechanisms in Low Pressure Capacitively Coupled Discharges**, ***G.F. Franz,*** University of Applied Sciences, Germany; *M.K. Klick,* Advanced Semiconductor Instruments, Germany

The dominating excitation mechanisms in capacitively coupled discharges are ohmic heating (mainly to electrons in the bulk, and, at high powers, also to the ions in the sheath) and stochastic heating (thermalization of the electric energy of the sheath). The latter process will gradually enhance its importance when the discharge pressure is reduced below a threshold value of about 100 mTorr. That means that the electron energy distribution function (EEDF) in this regime will be governed by stochastic heating. This is also the pressure range in which reactive ion etching takes place. Measurements with self-excited electron resonance spectroscopy (SEERS) in various plasmas reveal that stochastic heating will strongly depend on the nature of the gas (atomic or molecular, electronegative or electropositive). Since ohmic heating scales with discharge pressure whereas stochastic heating is nearly pressure independent, both the heating mechanisms can be separated. New results are presented which have simultaneously measured with VI- and Langmuir probes as well as with optical emission spectroscopy (OES) with traces of rare gases and are eventually compared with models created by Lieberman, Godyak, and Klick.

2:20pm **PS-WeA2 Influence of Frequency on the Characteristics of UHF Capacitively Coupled Plasmas in a 300 mm Chamber**, ***G.A. Hebner***, *E.V. Barnat, P.A. Miller,* Sandia National Laboratories; *A.M. Paterson, J.P. Holland, T. Lill,* Applied Materials, Inc.

We have investigated the characteristics of UHF capacitively coupled plasmas produced in a modified Applied Materials chamber. The chamber had a 14-inch diameter upper electrode (source) that was driven at 10 to 160 MHz and a 300 mm diameter electrostatic chuck with a ceramic process kit that was driven at 13.56 MHz (bias). Diagnostics employed include a microwave interferometer to measure the line-integrated electron density, a hairpin microwave resonator to measure the spatially resolved electron density, absorption spectroscopy to determine the argon metastable temperature and density, laser induced fluorescence (LIF) to determine the spatial distribution of the excited species, and spatially resolved optical emission. We found that for constant source rf power, the electron density increased with rf frequency. The argon 1s5 metastable temperature was slightly above room temperature (300 â?" 400K), significantly cooler than our previous measurements in inductively coupled plasmas. The metastable density was not a strong function of source frequency or rf power. The metastable spatial distribution was always peaked in the center of the chamber and had a weak dependence on frequency. Scaling of the plasma parameters with frequency, power and pressure, and implications to energy deposition models will be discussed. This work was supported by Applied Materials and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energyâ?Ts National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:40pm **PS-WeA3 Monitoring Electron Density of Processing Plasmas Using a Transmission-line Type Microwave Sensor**, *C.H. Hseih,* National Tsing Hua University, Taiwan; ***K.C. Leou,*** National Tsing Hua University, Taiwan, ROC; *C. Lin,* National Tsing Hua University, Taiwan

The purpose of this study@footnote 1@, was to develop an electron density sensor for applications in process real-time feedback control of plasma based semiconductor fabrication tools, such plasma etchers or PECVDs. The sensor was a dielectric waveguide based transmission-line where microwave propagates at a phase velocity determined by the structure and the plasma density (electron density) surrounding the structure. Thus the variation of plasma density can be estimated from the phase shift of the transmitted microwave from one to the other end of the transmission-line. For the proof-of-principle study, a coaxial type transmission-line was adopted with a Teflon outer dielectric and a copper inner conductor operated at a freqeuncy of 2-3 GHz. Analytical analysis of dispersion characteristics of the transmission line structure was carried and the resulting propagation constants were in good agreement with results from calculation using a commercial high frequency structure simulation code (HFSS by ANSOFT). Experimental demonstration have been performed with an inductively-coupled plasma. The sensor was mounted on the inner wall of plasma chamber with a coaxial line length of 8 cm and a distance of 5 cm between input and output ports. Measurement results show that the dependence of electron density of plasma source RF power predicted by the sensor agrees well with the Langmuir probe measurements. Compared to conventional microwave interferometers where line-averaged plasma density is measured, the trainsmission-line type microwave sensor will be less susceptive to the interference caused by multi-passes reflection/refraction effect resulting from nonuniformity of plasma density profiles. Therefore, it provides a measurement of higher sensitivity and wider dynamic range. @FootnoteText@ Work supported by the grant from the National Science Concil of R.O.C. under contract #92-2218-E-007-018.

3:00pm **PS-WeA4 Real-time Monitoring of Charge Accumulated during SiO@sub 2@ Etching using Pulse-Time-Modulated-Plasma**, ***Y. Suzuki***, *T. Shimmura, S. Samukawa,* Tohoku University, Japan

High aspect ratio SiO@sub 2@ contact hole etching is crucial for ULSI device fabrication. However, serious problems, such as charge-build-up damage, etching stops and microloading effect, mainly caused by charge accumulated in contact holes are not clearly solved. Therefore, it is very important to measure the amount of charges and to control such charge accumulated. In this paper, we monitored the amount of charge accumulated in real-time during the continuous wave (CW) and pulse-time-modulated (TM) plasma etching for a number of contact holes by using on-wafer monitoring device. This sensor consists of Poly-Si (300nm) / SiO@sub 2@ (1.7 µmm) / Poly-Si (300nm) layered structure on Si substrate. The diameter of contact holes was 300nm, the numbers of that were 6,400,000 and aspect ratio was 5.7. The potential differences between the top and bottom Poly-Si electrodes were measured during plasma discharge. In the case of TM plasma, the potential differences drastically reduced, compared to the CW plasma. The time-resolved measurement showed the potential differences were increased during a few tens of micro-seconds of pulse-on-time and was reduced during a few tens of micro-seconds of pulse-off-time. As the charge accumulated were saturated at the time constant of milli-seconds on the substrate surface, theresult suggests that a few tens micro-seconds TM plasma can drastically reduce the charge accumulated on the surface. The proposed on-wafer monitoring sensor can realize the real-time measurement of charge accumulated during the plasma etching processes.

3:20pm **PS-WeA5 The Use of the Radio Frequency Matching Network As a Diagnostic for Plasma Processing Chambers**, ***J. Caughman,*** *G.L. Bell,* Oak Ridge National Laboratory; *V. Resta,* Hewlett-Packard

Radio frequency (RF) power is commonly used in the plasma processing of semiconductors. As part of the RF system, many of the plasma processing chambers use RF matching networks with two variable tuning elements to transform the impedance at the chamber interface to be 50 ohms at the input of the matching network. The matching network is a highly tuned circuit, and the positions of the tuning elements are directly related to the RF impedance of the chamber. Thus, the positions of the tuning elements can be used as a diagnostic to determine processing sensitive parameters. Matching networks have been characterized to relate tuning element positions to the RF impedance and the power efficiency of the network. After characterization, the impedance and efficiency can be determined as a function of processing parameters simply by measuring the tuning element positions during processing. The technique has been demonstrated on both inductively coupled plasmas (ICP) and capacitively coupled plasmas (CCP). It has been found that the impedance is sensitive to changes in power, pressure, gas composition, and wall conditions. For example, an increase in ICP source power will cause an increase in the plasma density, which can be seen as an increase in the real part of the source impedance and a decrease in the real part of the bias impedance. The technique has been used on several different chambers and has been demonstrated to be helpful in terms of troubleshooting and chamber matching. Details of the characterization technique and the sensitivity of the impedance to processing conditions will be presented.

3:40pm **PS-WeA6 Measurements and Consequences of Non-Uniform RF Plasma Potential due to Surface Asymmetry in Large Area RF Capacitive Reactors***, **L. Sansonnens**, L. Derendinger, C. Hollenstein, A.A. Howling, H. Schmidt,* Ecole Polytechnique Fédérale de Lausanne, Switzerland*; J.P.M. Schmitt, E. Sakanaka,* UNAXIS-France SA, France

In small area capacitive reactors, the RF and DC plasma potential can be assumed to be uniform over the reactor area, and asymmetry between the grounded and powered electrodes leads to the well-known area law for determining the uniform DC and RF voltage amplitude across both plasma sheaths. In large area reactors, however, the RF plasma potential can vary over a long range across the reactor area due to the finite plasma conductivity. A local asymmetry of electrode area due, for example, to the lateral grounded walls for plasma confinement, causes a local RF plasma potential perturbation which propagates along the resistive plasma between capacitive sheaths. This propagation can be described by a telegraph equation for which a typical damping length can be determined. In this way, for a non-symmetric reactor wider than the damping length, the RF sheath voltage amplitudes which are unequal close to the reactor edges tend to be the same in the centre as for a symmetric reactor. A predicted consequence of this non-uniform RF plasma potential is the presence of non-ambipolar current circulating through the plasma and along conducting electrodes. In this work, we present measurements of the RF plasma potential and DC net current distribution over the grounded electrode of a large area reactor (57 x 47 cm@super 2@) using an array of surface probes, for various reactor geometry configurations. These experimental results are compared with a two-dimensional solution of the telegraph propagation model. Finally, we present some effects of the non-uniform RF plasma potential such as non-uniform power dissipation in the plasma which have important consequences for plasma processing.

4:00pm **PS-WeA7 Radiofrequency Discharge and Sheath Structure Around Dissimilar Surfaces***, **E.V. Barnat**, G.A. Hebner,* Sandia National Laboratories

Discontinuities present on a surface introduce perturbations to both the field and excitation around the discontinuity. Spatially resolved electric fields in an argon sheath near the discontinuous surfaces were measured using laser-induced fluorescence-dip spectroscopy (LIF-dip) while excitation is measured by LIF, optical emission and a Langmuir probe. Spatial maps of the electric field and excitation were obtained in the regions near these discontinuities as functions of power and pressure of the discharge. These measurements demonstrate the degree and extent of perturbation introduced into the plasma. Surface discontinuities investigated included metal-dielectric, metal-metal and metal-step junctions. 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 Energyâ?Ts National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:20pm **PS-WeA8 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.

4:40pm **PS-WeA9 Investigation of Correlation between Etching Profiles and Neutral Density in Cl@sub 2@/O@SUB 2@ Plasmas***, **M. Mori**,* Hitachi Ltd., Japan*; G. Cunge, M. Kogelschatz,* CNRS/LSP, France*; L. Vallier,* CNRS/LTM, France

Cl@sub 2@/O@sub 2@ plasmas are basically used in Shallow Trench Isolation (STI) etching of ULSI device fabrication. In STI etching, precise taper angle control is one of the issues for good coverage without stress damage to Si substrate at following deposition process. The taper angle is determined by the sidewall passivation layer during etching. Hence etching by-products (SiCl@sub x@) are thought to play an important role in taper angle control, because they are believed to be the precursors to the deposition of sidewall passivation layers. In this study, we have investigated the correlation between SiCl@sub x@ density and etching profiles in Cl@sub 2@/O@sub 2@ plasmas. The SiCl@sub x@(X=0-2) absolute densities are measured by UV broad band absorption spectroscopy. The thickness of the sidewall passivation layer is measured by comparing the etched profiles before and after removal of the passivation layer. The SEM results firstly confirm that good correlation between the taper angles and the thickness of the passivation layer on feature sidewalls over a wide range of plasma operating conditions (pressure, source power, O@SUB 2@ flow rate and total gas flow rate). By contrast, there is no correlation between the thickness of sidewall passivation layers and the SiCl@sub x@ densities in the plasma. For example, the passivation layer thickness increases rapidly while the SiCl@sub x@ density decrease with increasing O@SUB 2@ gas flow. Indeed, our data suggests that the growth rate of sidewall passivation layers is limited only by the O density in the plasma, which thus controls the etching profile. By roughly calculating O atom density as a function of electron temperature and density, we are then able to explain the trend of passivation layer thickness with pressure and source power. The role of O is to oxidize SiCl@sub x@ species chemisorbed on the surfaces exposed to the plasma, which, without oxidation are etched back into the plasma by Cl atoms.

5:00pm **PS-WeA10 2D-Imaging Measurements of Sputtered Atom Velocities in dc Magnetron Discharges by Doppler-Shifted LIF***, **K. Sasaki**,* Nagoya University, Japan*; K. Shibagaki,* Suzuka National College of Technology, Japan*; N. Nafarizal, H. Toyoda, T. Kato, S. Iwata, S. Tsunashima, H. Sugai,* Nagoya University, Japan

In the deposition of multilayer magnetic thin films such as Co/Pt and Fe/Pt using magnetron sputtering discharges, a key issue is how to obtain very flat interfaces between the multilayers. Bombardment of energetic ions and neutrals during deposition may roughen the interface. Understanding on energies of particles supplied to the substrate is helpful to optimize the apparatus for the deposition of multilayer magnetic films. In the present work, we measured the spatial distribution of velocity distribution of Fe atoms in a conventional dc magnetron discharges. We employed laser-induced fluorescence imaging spectroscopy. By recording pictures of laser-induced fluorescence at various wavelengths of a tunable optical parametric oscillator, we obtained many Doppler spectra that represent the velocity distributions of Fe atoms in a r-z plane of the cylindrically symmetric magnetron discharge. In a low-pressure discharge at 3 mTorr, Fe atoms near the target had broad velocity distribution, and they contained energetic component with velocity faster than 10 km/s (29 eV). At a distance of 60 mm from the target, Fe atoms had a thermalized distribution having two temperatures. By integrating the velocity distribution, we obtained two-dimensional maps of the mean velocity of Fe atoms. In a low gas pressure of 3 mTorr, Fe atoms had a mean velocity of 3.6 km/s in the region adjacent to the target surface. In a gas pressure of 20 mTorr, the mean velocity of Fe adjacent to the target was slower than 1 km/s. This work was supported by the 21st Century COE Program by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Plasma Science and Technology
Room 213A - Session PS-ThM
Atmospheric and Microdischarges

Moderator: L. Bardos, Uppsala University, Sweden

8:20am **PS-ThM1 Atmospheric and Micro Discharges***, **J.K. Lee**,* Pohang University of Science and Technology, South Korea, S. Korea*; S.S. Yang, M. Radmilovic-Radjenovic,* Pohang University of Science and Technology, South Korea*; S. Mukherjee,* Pohang University of Science and Technology, South Korea, S. Korea **INVITED**

Plasma display panels (PDPs) are micro discharges, operated at high pressures of 400-500 Torr. Using 2-D kinetic simulation code (XOOPIC), we calculated incident angle and energy distributions of ions on the cathode surface in a PDP cell. Kinetic results show that in a coplanar-type PDP cell, most ions impinge on the MgO surface at the cathode region with the incident angle in the range of 10~30 degrees@footnote 1@ from normal with energies below 50 eV and two temperatures 5 and 50 eV. The calculated electron temperature at the anode striation@footnote 2@ region is lower than that between the striation bunches and ranges from 0.5 to 2 eV. We operated the panel at pressures in atmospheric range to study the distinction in the characteristics of the discharge. At a constant pd value by increasing pressure p (in the atmospheric pressure range) and reducing gap length d, we observed similar discharge characteristics to the conventional PDP. We also investigated the difference in the discharge characteristics in the presence and absence of radiation trapping@footnote 3@ and dimers by our 2-D and 3-D fluid simulations and the Paschen breakdown characteristics of microdischarges at high pressures. @FootnoteText@ @footnote 1@ S.S. Yang, J.K. Lee, et al., Contri. to Plasma Phys. (to appear in 2004).@footnote 2@ C.H. Shon and J.K. Lee, Phys. Plasmas 8, 1070 (2001).@footnote 3@ H.C. Kim, S.S. Yang, and J.K. Lee, J. Appl. Phys. 93(12), 9516 (2003).

9:00am **PS-ThM3 Gas and Electrode Temperatures in Non-equilibrium Atmospheric Pressure Plasma with Microwave Excitation***, **M.N. Nagai**,* Nagoya University, Japan

Gas and Electrode Temperatures in Non-equilibrium Atmospheric Pressure Plasma with Microwave Excitation Plasma processing is the most attractive industrial technology because etching, deposition, or synthesis processings of materials are able to be performed at the low temperature. Recently, atmospheric pressure non-equilibrium plasmas expand the application in not only conventional but also new industrial and science fields. To produce non-equilibrium plasmas, several attempts have been proposed, such as corona discharges and dielectric barrier discharges. The neutral gas temperature is one of the most important plasma parameters for producing non-equilibrium atmospheric pressure plasma. The gas temperature measured gives us the information concerning the chemical reaction in the plasma such as combination and elimination reaction. Excess high gas temperature causes the evaporation of electrodes for producing the plasma, and the melting of materials by the plasma irradiation. In this study, non-equilibrium atmospheric pressure plasma was successfully produced in N@sub 2@, Ar, or He gas using a dielectric barrier micro-gap plasma with microwave excitation. We investigated effects of pulse discharge and electrode temperature on gas temperature. We measured gas temperature by N@sub 2@ optical emission of the second positive band system and electrode temperature by blackbody emission. It was found that the short pulse modulation of microwave power and water-cooled electrode were effective for reducing the gas temperature. The pulse discharge decreased the gas temperature from 900 K to 600 K, and the water-cooled electrode decreased the gas temperature by more than 200 K. Controlling of the electrode temperature was one of the most effective techniques to reduce the gas temperature because the gas temperature was in equilibrium with the electrode temperature.

9:20am **PS-ThM4 Characterization of the Cold Atmospheric Plasma Hybrid Source***, L. Bardos, **H. Barankova**,* Uppsala University, Sweden

Parameters of the Hybrid Hollow Electrode Activated Discharge (H-HEAD) source for cold atmospheric plasma applications will be described. 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 nozzle by pulsed DC power. The source is capable to produce over 15 centimeters long plasma plume at less than 500 sccm of the argon flow in open air and the microwave power of 500 W (2.4 GHz). Parameters of the hybrid plasma are controlled by both the microwave power and the power delivered to the hollow cathode. An anomalous effect of local maximum in the length of plasma plume at low gas flows is described. Results of the optical emission spectroscopy in argon and neon and electrical parameters of the hybrid discharge will be presented.

9:40am **PS-ThM5 Diagnostics of High Pressure DC Helium Microplasma Discharge***, **Q. Wang**,* University of Houston*; I. Koleva,* University of Sofia, Belgium*; D.J. Economou, V.M. Donnelly,* University of Houston

Gas and plasma diagnostics were performed in a slot-type DC microplasma (200 microns gap) discharge at high pressures. The gas temperature in a helium discharge was estimated by adding small quantities of nitrogen (<100 ppm) into the gas feed. Specific vibrational bands (v'v"), namely (1,3), (0,2) and (1,4) of the N@sub 2@ second positive system, were carefully selected to avoid interference with emission from He atoms and He@sub 2@ excimer. At 250 Torr pressure and 200 mA/cm@super 2@ current density, the gas temperature was T@sub g@ = 350 ± 25 K. The measured gas temperature was almost independent (to within experimental uncertainty) of pressure (in the range of 150 Torr - 600 Torr), and current density (in the range of 100 mA/cm@super 2@ - 400 mA/cm@super 2@). These measurements were consistent with a simplified heat transfer model. Spatially resolved measurements of electron temperature were also performed using trace rare gas optical emission spectroscopy (TRG-OES). These measurements are greatly complicated by collisional quenching at the high operating pressures. Electron density and electron temperature profiles was deduced by comparing emission intensities from the Paschen 2p@sub x@ (x = 1-10) manifold of Ne, Ar, Kr and Xe trace gases. Results suggest that the electron temperature peaks in the cathode sheath region, while the plasma density peaks away from the cathode sheath. A self-consistent fluid model of a DC helium microdischarge was in agreement with the experimental data. Work supported by DOE/NSF.

10:00am **PS-ThM6 Atmospheric-pressure Microdischarges as Short-residence Time Reactors for Silicon Nanoparticle Synthesis***, **R.M. Sankaran**[1], D. Holunga, R.C. Flagan, K.P. Giapis*, California Institute of Technology

Microdischarges are investigated as short-residence time reactors for the synthesis of nanoparticles. The application is attractive since nucleation and growth can be limited in the reaction zone, while charging of particles in the plasma may reduce coagulation downstream. We report here on the gas-phase synthesis of silicon nanoparticles in an atmospheric-pressure dc microdischarge. The discharges are formed in silane/argon gas mixtures between a metal capillary tube (d=180 microns) that serves as the cathode and an anode tube of larger size. Incorporation of gas flow through the discharge results in a continuous production of aerosol particles which are size classified in situ using a radial differential mobility analyzer (RDMA). Based on their electrical mobility, the particles were found to possess relatively narrow distributions (@sigma@@sub g@=1.3-1.5) with mean sizes between 2 and 5 nm depending on reactor conditions. Electrical measurements after synthesis in the microreactor show that the particles are charged both negatively and positively. To further characterize the particles, the aerosol stream is bubbled into solvents directly after synthesis in the microreactor. These colloidal dispersions exhibit strong blue photoluminescence with maximum intensity at 440 nm (2.8 eV). Atomic force microscopy on solutions drop cast on silicon substrates have verified that the particles are as small as 2 nm. In this talk, we will discuss features of this new synthesis technique including effects of discharge conditions on particle growth and optical properties.

10:20am **PS-ThM7 Comparison of Atmospheric Pressure Helium Plasmas Operating in the Abnormal Glow and Recovery Modes***, R.F. Hicks, **X. Yang**[2], M. Moravej, G. Nowling,* University of California, Los Angeles*; S. Babayan, J. Penelon,* Surfx Technologies

The properties of a radio-frequency atmospheric pressure plasma fed with helium and nitrogen were investigated. Two discharge modes were identified with current-voltage measurements and optical emission spectroscopy. After the discharge was struck, the plasma entered an abnormal glow regime with a maximum power density of 4.8 W/cm@super 2@, corresponding to a current density and voltage of 0.73 A/cm@super 2@ and 317 V. Further increasing the power caused the plasma to shift into a new "recovery" mode with a dramatic reduction of current and voltage and a surge in power to 416 W/cm@super 2@. This transition is attributed to sheath breakdown. The spatial emission intensity between the electrodes in the abnormal glow reached a maximum 0.25 mm away from

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

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

the electrodes. In contrast, the recovery mode exhibited maximum emission intensity at the edge of the electrodes, with an intensity 200 times higher than that of the abnormal glow. The neutral gas temperature measured in the abnormal and recovery modes equaled 75 and 250 °C, respectively. The density of nitrogen atoms produced in the plasma was determined by measuring the temporal decay rate of the first-positive emission of nitrogen molecules, i.e., N@sub 2@(B) @super __@> N@sub 2@(A) + h@nu@. It was found that with 0.4 vol.% N@sub 2@, the abnormal and recovery modes produced 1.0x10@super 16@ and 1.7x10@super 16@ cm@super -3@ N atoms at maximum power densities of 4.8 and 416 W/cm@super 2@, respectively. These results indicate that the abnormal glow is more efficient at dissociating molecules into reactive species. A thorough discussion of the physics and chemistry of the atmospheric pressure plasma will be provided at the meeting.

10:40am **PS-ThM8 Atmospheric He-O@sub 2@ DBD Plasma for Steel Decontamination***, **E. Michel,*** Universite Libre de Bruxelles, Belgium*; E. Silberberg,* Arcelor Group*; F. Reniers,* Universite Libre de Bruxelles, Belgium

The use of a DBDs allows the stabilization of cold plasmas at atmospheric pressure which are of a great interest for industrial surface treatments because they do not request expensive vacuum systems. Contrary to wet treatments traditionally used to clean steel surfaces, the plasma treatments are environmental friendly, as they do not produce toxic waste. Standard steel surfaces were covered with various amounts of oil using dip coating. The contaminated surfaces were treated using atmospheric pressure plasma in a DBD. In our configuration, the hot electrode only is covered with the dielectric, whereas the other electrode being the sample. Voltages between 1 to 4 kV were applied between the electrodes, at a frequency varying between 5 and 30 kHz. The plasma gas consisted in a mixture of He-O@sub 2@ (2 to 10 % oxygen), at atmospheric pressure. The plasma chemistry was characterized using optical emission spectrometry (OES). The electrical characteristic of the plasma were recorded as a function of the applied voltage, frequency and gas composition. The transition parameters between the homogenous glow discharge and the filamentary one were established for our configuration. The kinetics of decontamination was studied by Auger electron spectroscopy (AES) and infrared spectroscopy (IRRAS- FTIR). The effect of the frequency, the applied voltage, the discharge current, the initial amount of contamination and the plasma gas composition on the kinetics of oil degradation was studied and discussed. The resulting surface state of steel was investigated using AES and X-ray photoelectron spectroscopy. Finally, a macroscopic model for the kinetics of decontamination of steel surfaces by He-O@sub 2@ atmospheric plasmas is proposed.

11:00am **PS-ThM9 Line Plasma Generation of Microwave Employing Narrow Width Waveguide***, T. Fukasawa,* Tokai University, Japan*; S. Fujii,* ADTEC Plasma Technology Co., Ltd., Japan*; **H. Shindo,*** Tokai University, Japan

Line plasma over 40 cm in length has been required for large area plasma processing at relatively higher pressure or atmospheric pressure. The line plasma will be applied to surface treatment of rolled organic thin film; furthermore, processing of large area flat panel such as large area LCD. The width of conventional rectangular waveguide is about 10 cm, therefore wavelength(@lambda@g) in the waveguide is about 15cm. However, the @lambda@g is increased with the decrease of the width of the waveguide. @lambda@g = @lambda@/@sr@(1-@lambda@/2W)@super 2@. @lambda@ is wave length in free space and W is width of the waveguide. We manufactured very narrow rectangular waveguide, whose inner widths are 63.5mm, 61.8mm and 61.5mm, respectively. Length and inner thickness of the waveguide are 500mm and 5mm respectively. 2.45 GHz microwave was introduced to the narrow waveguide through TE mode rectangular waveguide (BRJ-2), three-stub tuner and rectangular tapered waveguide. Electric field in the narrow waveguide was measured using electric probe. Measured @lambda@g was corresponded to the above-mentioned formula. @lambda@g was over 1m at the waveguide width of 61.5mm. A slit was made on the side of the wave-guide of 400mm in length and 1mm in width. A quartz tube was set on the slit, whose inner diameter and outer diameter were 3mm and 4mm, respectively. Length of the quartz tube was 400mm. He gas was introduced into the quartz tube. Pressure was measured by capacitance manometer. At the microwave power of 200W, some sections were observed corresponding to wavelength of microwave in free space. At the microwave power of 1kW, however, uniform optical emission intensity was achieved. Optical emission spectrum (OES) intensity at the wavelength of 656nm was measured in order to measure the distribution of electron density in the quartz tube. At the microwave power of 1kW, uniformity of the OES intensity was +-8.4%.

11:40am **PS-ThM11 Atmospheric Pressure Plasma Liquid Deposition - A New Route to High Performance Coatings***, **S.R. Leadley**, L. O'Neill, L.-A. O'Hare, A.J. Goodwin,* Dow Corning Ltd., Ireland

Plasma enhanced coating processes are well known as a route to well adhered, conformal, high performance coatings. Dow Corning Plasma Solutions has developed a new coatings approach, which was invented in collaboration with the Department of Chemistry of the University of Durham, UK. Atmospheric Pressure Plasma Liquid Deposition combines atmospheric pressure glow discharge (APGD) technology with a unique precursor delivery system. This process operates at atmospheric pressure and ambient temperature allowing the use of a wide range of liquid precursors. The plasma causes polymerization of the precursor so that it is deposited as a conformal, well-adhered thin-film coating, which retains all the functionality and value of the original liquid monomer precursor. This technology retains flexibility with respect to process chemistry and the capability to deliver a vast range of surface functions through the mixing and matching of precursors. The aim of this presentation is to introduce the technology behind this new process and show examples of coatings that have been prepared using mixed monomers, so that the properties of the coating can be tailored.

Dielectrics
Room 304B - Session DI+PS-ThA

Oxides on Semiconductors
Moderator: S.A. Chambers, Pacific Northwest National Laboratory

3:40pm **DI+PS-ThA6 Crystalline Oxides on Semiconductors, from Interface Structure to Electrical Properties**, ***F.J. Walker,*** University of Tennessee; *C.A. Billman,* Penn State University; *M. Buongiorno-Nardelli,* North Carolina State University; *R.A. McKee,* Oak Ridge National Laboratory **INVITED**
From the point of view of synthesis using molecular beam epitaxy (MBE) and understanding using tools developed from first principle theory like density functional theory (DFT), a metal oxide semiconductor (MOS) device can be described as an epitaxial superlattice where each atomic layer is well-defined. This view is becoming increasingly germane to device physics as dimensions are scaled down to the atomic level. In this paper we discuss the fundamental interplay of the physical structure, as determined by reflection high energy electron diffraction (RHEED), and the electrical properties, as determined by frequency-dependent electrical impedance measurements and x-ray photoelectron spectroscopy (XPS), for the crystalline oxide on semiconductor system. We show that an interface phase is particularly important to structure and electrical properties for alkaline earth oxides grown on silicon and germanium. The interface phase begins as a surface phase of strontium silicide and transforms to an interface phase through a structural transition. The final structure and composition of the interface phase determines the band offset, interface state density and serves as a template for the epitaxial growth of the alkaline earth oxides. Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory under contract DE-AC05-00OR22725 with UT-Battelle, LLC and at the University of Tennesssee under contract DE-FG02-01ER45937.

4:20pm **DI+PS-ThA8 Ultra Thin Oxides and Nitrides on Si: Growth and Properties**, ***P. Morgen***, *U. Robenhagen, A. Bahari,* SDU Odense, Denmark; *M.G. Rao,* IISc, India; *K. Pedersen,* Aalborg University, Denmark
Various conditions for slow growth of ultra thin silicon oxides on Si have been studied, at relatively low temperatures and pressures, in an ultra high vacuum environment. In this way a hitherto unknown regime in pressure-temperature space has been discovered including a fast (ballistic) stage terminating with a self-limiting oxidation. This precedes and deviates radically from the high temperature-high pressure Deal-Grove mechanism. Several different schemes are invented leading to oxide thicknesses from about 0.4 to 0.7 nm, with high quality of the interface and uniformity of coverage. Our present and previous studies connect the initial steps of oxygen adsorption and reaction at room temperature with the first steps (and barriers) to form three dimensional oxides on two Si surfaces (111) and (100). The structural information is obtained by following these oxidation reactions with photoemission spectroscopy, including high resolution, surface sensitive core-level photoemission; STM; LEED; optical second harmonic generation spectroscopy, and Auger electron spectroscopy. Similar procedures are followed to create ultra thin nitrides using microwave dissociated nitrogen. This process is already known to be self limiting, but at a somewhat higher film thickness than for the growth of oxides. The prospect of doping these oxides with nitrogen, and these nitrides with oxygen, is also successfully explored.

4:40pm **DI+PS-ThA9 Preparation and Properties of Clean Si@sub 3@N@sub 4@ Surfaces**, ***V.M. Bermudez***, *F.K. Perkins,* Naval Research Laboratory
Si@sub 3@N@sub 4@ is an important material for use in electronic devices. Thin films of Si@sub 3@N@sub 4@ are used as passivation layers and diffusion barriers in IC's and as protective coatings in disk drives. However, the basic surface science of Si@sub 3@N@sub 4@ films has been impeded by the difficulty in obtaining a clean and undamaged surface. In this work, in-situ chemical methods for preparing atomically clean surfaces of Si@sub 3@N@sub 4@ thin films in UHV have been studied using XPS, UPS, ELS and AES. Prior to UHV studies, the thin films (grown ex situ on Si(100) by LPCVD) were characterized by IR reflection-absorption spectroscopy which showed them to be stoichiometric with a low H content. A two-step process consisting of annealing in a flux of NH@sub 3@ vapor to remove C and vapor deposition of Si (followed by thermal desorption) to remove O is found to be an effective cleaning procedure. Other potential cleaning methods, such as annealing in UHV without in- situ chemical treatment or annealing in a flux of H atoms, were considered and found to be only partly effective. The clean surfaces are disordered, as seen in LEED, but show no evidence of Si-Si bonding (which would indicate N vacancies) in the Si LVV AES or in surface-sensitive Si 2p XPS. Evidence for surface- related features is seen in the N 1s XPS and in ELS data in the region of valence excitations; however, no indication of occupied surface states near the valence band maximum is seen in UPS. Preliminary results for O@sub 2@ chemisorption show adsorbate- induced features in the band gap and also evidence for a reduction in the negative surface potential due to electron traps present on the clean surface.

5:00pm **DI+PS-ThA10 STM, STS, and DFT Studies of SiO Deposition on the Ge(100) Surface**, ***T.J. Grassman***, *J.Z. Sexton, A.C. Kummel,* University of California, San Diego
To further the development of a germanium-based metal-oxide-semiconductor field effect transistor (MOSFET) a suitable gate-oxide material must be found which yields a high-quality, electrically-unpinned interface. For this, the semiconductor/oxide interface needs to be free of charge traps and other such interfacial defects that can cause Fermi-level pinning. High defect densities reduce the capacitance of the MOS structure and prevent the modulation of the semiconductor valence and conduction bands via the application of a gate bias. Germanium's intrinsic oxide has been shown to be inadequate for the task of providing a clean interface, therefore an alternative material must be used which can be deposited and grown on the Ge surface. To this end, we are investigating the bonding and electronic structure of the interface between SiO and the Ge(100)-p(2x1) surface using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) computational modeling. SiO can act as a precursor to SiO@sub 2@ or as a buffer layer for high-k dielectric growth. We will present atomically resolved images of both the clean Ge(100) and SiO-deposited surfaces at various coverages, along with DFT modeling results of the observed bonding structures. We find that SiO always bonds Si-end down, mostly inserting in between the Ge dimer rows and sometimes into the Ge dimers themselves. Even at modest coverages (> 5%) SiO bilayers are formed via pyramidal (SiO)@sub 3@ molecular structures with Si-O-Si-O bonding configuration. DFT-based STM simulations will be presented to aid in the interpretation of experimental STM images. We will also present STS dI/dV spectra of the associated surface electronic structure (density of states) which show that the SiO/Ge interface yields an unpinned Fermi level.

Plasma Science and Technology
Room 213A - Session PS-ThA

Plasma-Surface Interaction
Moderator: G.F. Franz, University of Applied Sciences, Germany

2:00pm **PS-ThA1 A Comprehensive Study of Gas Phase and Plasma-Surface Interactions of Depositing Fluorocarbon Plasma Systems**, ***I.T. Martin***, *E.R. Fisher,* Colorado State University
A thorough investigation of the gas-phase chemistry, plasma-surface interactions, and surface properties of deposited materials has been performed for C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas. OES-actinometry, LIF and MS were used to study the plasma gas phase. OES quantifies excited state species in these systems, whereas LIF measurements provide relative densities of ground state CFx species as a function of applied rf power (P) and pressure. CF LIF excitation spectra were used to measure CF rotational temperatures (@Theta@@sub R@) as a function of P and pressure: @Theta@@sub R@(CF) in C@sub 4@F@sub 8@ plasmas is approximately constant over a range of P and pressure, whereas it increases with P in the C@sub 3@F@sub 8@ systems. MS data identify nascent ions and measure ion energy distributions. Plasma-surface interactions of CFx species were investigated using our Imaging of Radicals Interacting with Surfaces (IRIS) molecular beam apparatus. CF@sub 2@ surface production was characterized during C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasma processing of Si via a scattering coefficient, S(CF@sub 2@), the ratio of CF@sub 2@ molecules scattering from the surface relative to those in the molecular beam. S(CF@sub 2@) values>1 were measured during the deposition of amorphous fluorocarbon (FC) materials. This net surface production of CF@sub 2@ suggests that CF@sub 2@ is not a deposition precursor in these FC systems. Charged species contribute to CF@sub 2@ surface production, as demonstrated by the decrease in S(CF@sub 2@) measured under ion-limited conditions. A notable result of this work is the positive correlation between S(CF@sub 2@) and %-crosslinking measured by XPS in the deposited FC materials. Optimized FC materials were used in several applications, including the

production of micropatterned surfaces used in cell growth studies, and the modification of microfluidic devices. The performance of our FC materials in these applications will be discussed.

2:20pm **PS-ThA2 Mechanisms of Etching in the Presence of Depositing Species: Molecular Dynamics Simulations of Silicon Etching in Fluorocarbon Plasmas***, **J.J. Vegh**, D. Humbird, D.B. Graves,* University of California, Berkeley

The fundamental mechanisms of plasma etching in the presence of depositing species, a very common situation in industrial practice, remains poorly understood at the atomistic level. Recent MD simulations of silicon etching in the presence of small FC ions and neutral radicals, F atoms, and Ar@super +@ have consistently failed to reproduce experimental observations of simultaneous Si etching and the presence of relatively thick FC film on the surface. Simulations of FC film formation alone, without Si etching, can easily be observed with small unsaturated FC ions at energies below about 100 eV, and thermal CF and CF@sub 2@ are observed to deposit alone or in the presence of low energy ion bombardment (@<=@50 eV). Si etching is observed in the presence of higher energy ions, especially Ar@super +@, and most readily in the presence of thermal F. However, the combination of significant Si etch, coupled with dominant FC signal in simulated surface XPS measurements, has proven elusive using only small FC species. Even at relatively high neutral to ion ratio (e.g. 90:9:1 CF/F/Ar@super +@), only a thin FC film develops during Si etch, and the XPS is dominated by the C-C/Si peak. We conclude that simultaneous FC film and Si etch requires heavier, unsaturated FC neutrals and/or ions. These large, polymeric species are created by ion impact or neutral F attack within a deposited FC film. In other words, the FC film can be etched in the form of large products that redeposit on the surface to maintain the film. We demonstrate that simultaneous FC film and Si etch requires that the FC film have minimal cross-linking and be relatively weakly bound to the surface. We highlight the role of ion impact in locally removing substantial amounts of FC film material, exposing the underlying Si to etch species.

2:40pm **PS-ThA3 Deposition and Composition of Polymer Films in Fluorocarbon Plasmas: CW and Pulsed Systems@footnote 1@***, **K. Rajaraman**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Fluorocarbon plasma etching is the primary method to obtain selectivity between dielectrics. Optimization of this etching technique becomes more critical as dielectrics thin. To first order, etch rates depend on thickness of the polymer layer, which controls the energy of ions striking the dielectric surface. However, the composition of the polymer determines the rate of deposition and sputtering of the film, as well as the rate of reaction of the polymer with the underlying dielectric. To address this compositional dependence, a surface chemistry model has been developed to resolve the polymer at a mesoscale level by treating CFx sites distinctly. In this manner, the fractional composition of the polymer film on a bond-to-bond basis can be resolved. This surface model was interfaced with a zero-dimensional plasma kinetics model (GLOBAL_KIN) and a 2-dimensional plasma equipment model (HPEM). Simulations were performed using the ICP reactor geometry and conditions from Li et al.@footnote 2@ We will discuss results for film compositions using different fluorocarbon gas chemistries (e.g., M/O@sub 2@/Ar, M = C@sub 2@F@sub 6@, CHF@sub 3@, c-C@sub 4@F@sub 8@). Due to the change in the pathways for generation of major free radicals, the fluorocarbon films formed in the chemistries investigated are qualitatively different, and to some degree reflect the fragmentation pattern of the feedstock gases. Changes in Ar concentration affect the amount of sputtering of the fluorocarbon films, and hence the film thickness. The consequences of pulsing the plasma on the fluorocarbon film structure will also be discussed. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF. @footnote 2@ Li et al., J. Vac. Sci. Technol. A 20, 2052 (2002)

3:00pm **PS-ThA4 Dangling Bond Creation and Annihilation during Plasma Processes Studied by In-situ ESR Technique***, **S. Yamasaki**,* AIST, Japan*; K. Ishikawa,* Tohoku University, Japan **INVITED**

To understand the surface chemical reactions of plasma processes, various probes have been introduced for monitoring. Defect creation and annihilation during plasma processes, whether at surface or in bulk, play an essential role in determining final device performances and chemical reactions. If one can directly observe the creation and annihilation of dangling bond (db) centers and those dynamic changes of bonding configurations during plasma processes in real-time, it will give important information for improvement of plasma processes. In this talk we introduce in-situ ESR measurements [1,2], detecting surface defects during H2 and Ar plasma treatments on hydrogenated amorphous silicon (a-Si:H) and in-line ESR measurements during fluorocarbon gas etching processes of SiO2. From these experimental results we report how the plasma species affect surface defect structure and discuss the surface chemical reactions. [1] K. Ishikawa, et al., Appl. Phys. Lett. 81, 1773 (2002). [2] S. Yamasaki, et al., Appl. Phys. Lett. 70, 1137 (1997).

3:40pm **PS-ThA6 NH@sub x@ Radical Densities and Plasma Chemistry in a Remote Ar-NH@sub 3@-SiH@sub 4@ Plasma for Silicon Nitride Deposition***, **P.J. van den Oever**,* Eindhoven University of Technology, The Netherlands, Netherlands*; J.H. van Helden, R. Engeln, D.C. Schram, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Although plasma deposited amorphous silicon nitride (a-SiN@sub x@:H) has widespread applications in industry, the exact growth mechanism of these films from NH@sub 3@-SiH@sub 4@ plasmas remains unclear. For example, the role of silane radicals, ammonia radicals, and possibly aminosilane radicals in the growth process is still not resolved. To obtain insight into the role of the various radicals in the plasma we have carried out absolute density measurements of NH and NH@sub 2@ radicals in a remote Ar-NH@sub 3@ and Ar-NH@sub 3@-SiH@sub 4@ plasma. The radicals have been detected by means of the cavity ringdown spectroscopy (CRDS) technique probing NH and NH@sub 2@ electronic transitions at ~597 and ~335 nm, respectively. The absolute densities obtained range from 10@super 10@ to 10@super 12@ cm@super -3@ depending on the NH@sub 3@ flow, downstream axial position, and the presence and flow of SiH@sub 4@. The kinetic gas temperature determined from Doppler broadening of the absorption lines is ~1500 K, in agreement with previous measurements. For the Ar-NH@sub 3@ plasma an increase of the NH and NH@sub 2@ density with the NH@sub 3@ flow has been observed. Analysis of the data on the basis of the reaction rates proposed in literature, suggests a considerable regeneration of NH@sub 3@ from its dissociation products. This possibly explains the high NH@sub 3@/SiH@sub 4@ ratio that is necessary to obtain a sufficiently high N/Si ratio in films deposited from Ar-NH@sub 3@-SiH@sub 4@ plasmas. The addition of SiH@sub 4@ decreases the NH@sub 2@ density in the Ar-NH@sub 3@-SiH@sub 4@ plasma and at low NH@sub 3@ flows even no NH@sub 2@ is observed. To understand these trends, which can originate both from plasma and surface processes, the NH density is currently investigated under the same plasma conditions. From a comparison of the results with those obtained from a simple plug-down model, insight into the key reactions in the Ar-NH@sub 3@-SiH@sub 4@ plasma is obtained.

4:00pm **PS-ThA7 First-Principles Analysis of Precursor-Surface Interactions Relevant to Plasma Deposition of Silicon Thin Films***, **T. Bakos**,* University of Massachusetts, usa*; D. Maroudas,* University of Massachusetts

Plasma-enhanced chemical vapor deposition is used widely for growing hydrogenated amorphous silicon (a-Si:H) thin films for electronic, optoelectronic, and photovoltaic applications. Plasma deposited film properties, such as H content, crystallinity, and surface roughness, depend on the identities and fluxes of reactive radicals impinging on the deposition surface and on the corresponding radical-surface interaction mechanisms. In this presentation, we report results of first-principles density functional theory (DFT) calculations that elucidate the reaction pathways and energetics of key reactions with the H-terminated Si(100)-(2x1) surface of the SiH@sub 3@ radical, the dominant precursor for deposition of device-quality a-Si:H films. In particular, we have found that SiH@sub 3@ can insert into surface Si-Si dimer bonds, abstract H from surface Si atoms through an Eley-Rideal (ER) mechanism and passivate surface dangling bonds in exothermic and barrierless reactions. In all of these cases, we have determined the optimal reaction pathways and the corresponding transition states based on accurate, well-converged total-energy calculations and implementing the nudged elastic band method. The theoretically predicted energetics of radical insertion, H abstraction, and passivation reactions are consistent with the experimentally observed temperature independence of the SiH@sub 3@ surface reactivity during plasma deposition of a-Si:H films. In addition to the ER mechanism, we have identified a Langmuir-Hinshelwood mechanism of surface H abstraction with a moderate energy barrier that may be responsible for reducing the H content of films deposited at high temperatures. Reactions similar to those analyzed by DFT on the Si(100)-(2x1):H surface also are observed in molecular-dynamics simulations of a-Si:H thin film growth. Therefore, our electronic-structure analysis also can be considered as representative of surface reactions occurring on a-Si growth surfaces.

4:20pm **PS-ThA8 Uniformity Study in Large-Area Showerhead Reactors***, **R. Sobbia**, L. Sansonnens,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; J. Bondkowski,* UNAXIS France SA, France

Large area plasma enhanced chemical vapour deposition of thin films such as silicon nitride or amorphous silicon is widely used for thin film transistor fabrication in the flat panel display industry. A numerical three dimensional model to calculate the deposition uniformity over the whole electrode surface for RF rectangular showerhead reactors powered at 13.56 MHz is presented. The simulation tool is a commercially-available finite-volume software (CFDRC ACE+) which solves the multi-species, multi-reaction chemistry in capacitively coupled plasma. In order to simplify the three dimensional geometry, the injected gas flow distribution across the showerhead is calculated separately and introduced as volumetric source terms for the gas flow and species continuity equations via a dynamic library coupled with the main Solver. The model is applied to the particular case of silicon nitride deposition and the results are compared with uniformity profiles obtained in an industrial PECVD reactor. Perturbations due to reactor edges together with non-uniform distribution of voltage, gas flow and chemical species are investigated as possible sources of the inhomogeneity of the thin-film.

4:40pm **PS-ThA9 Validity of Binary Collision Theory in Ion-Surface Interactions at 50-500 eV***, M. Gordon, **K.P. Giapis**,* California Institute of Technology

Ion-surface interactions in the 50-500 eV regime have become increasingly important in plasma processing. Profile evolution simulations rely on the binary collision approximation (BCA) to estimate the energy of scattered ions. Concerns exist in literature about the validity of the BCA theory at low impact energies because peculiarities are frequently seen in the scattered ion energy distribution. Sub-surface processes, multiple bouncing, and super-elastic phenomena have all been hypothesized. This talk will explore the usefulness of BCA theory in predicting energy transfer during ion-surface collisions in the 50-500 eV energy range. Well-defined beams of rare gas ions (Ne, Ar) were scattered off semiconductor (Si, Ge) and metal surfaces (Al, Mg, Ti, Ag, Au, Ni, Ga) to measure energy loss upon impact. The ion beams were produced from a floating ICP reactor coupled to a small accelerator beamline for transport and mass filtering. Exit energies were measured using a 90 deg electrostatic sector coupled to a quadrupole mass filter with single ion detection capability. Although the BCA presents an over-simplified picture of the collision process, our results demonstrate that it is remarkably accurate in the 50-500 eV range for a variety of projectile-target combinations. However, large deviations from BCA exist for combinations where electron promotions may occur during the hard collision. We find that to be the case for Si, Al, and Mg at energies greater than 500 eV. The promotion occurs at a target-dependent threshold energy and is surface mediated. Further, doubly-charged projectiles maybe generated during the hard collision at the same energy threshold. The implications of these findings for profile evolution during plasma etching will be discussed.

5:00pm **PS-ThA10 Molecular Dynamics Simulation for Physical Sputtering and Deposition of Pt and Au Films***, K. Ito,* Kyoto University, Japan*; H. Yamada,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; **S.H. Hamaguchi**,* Osaka University, Japan, Japan

Platinum (Pt) is often used as a material of choice for electrodes of submicron-scale capacitors in Dynamic Random Access Memory (DRAM) and other semiconductor devices. Gold (Au) is also used in various electronics applications due to its high conductivity and chemical stability. Since micron/sub-micron-scale etching of noble metals such as Pt and Au in semiconductor applications is usually done mostly by physical sputtering, a better understanding of the nature of beam surface interaction between non-reactive atoms and Pt/Au films may facilitate the development of better noble metal dry etching processes with higher controllability of micro-scale feature profiles. For this purpose, we have used molecular dynamics (MD) simulations to study Ar or Pt beam interaction with Pt substrates and also Ar or Au beam interaction with Au substrates, using classical inter-atomic potential functions based on the Embedded Atom Method (EAM). Especially of interest are estimates of sputtering yields/deposition rates of such processes as functions of beam energies and beam injection angles obtained from MD simulations. Some of the simulation results are in good agreement with known experimental results whereas others are qualitatively different from experimental observations although there have not been many beam experiments in the relatively low energy range that we are interested in. In this presentation, we shall present MD simulations data of the sputtering yields and deposition rates, compare those with known experimental data, and discuss possible sources of discrepancy between simulation and experimental data.

Plasma Science and Technology
Room 213C - Session PS+BI-FrM
Plasmas in Bioscience
Moderator: K. Seaward, Agilent

8:20am **PS+BI-FrM1 X-Ray and Neutron Reflectivity Studies of Plasma Polymer Coatings***, S.K. Øiseth,* Unaffiliated*; P.G. Hartley, **K.M. McLean**,* CSIRO Molecular Science, Australia*; A Nelson, M James,* Bragg Institute, Australia

Plasma polymer coatings adhere to and contour the surfaces of most organic and inorganic materials, and are attractive as surface chemical modification systems, since they offer both robustness and inherent surface chemical functionality for further surface chemical derivatisation. A variety of different techniques have been used to characterise the physico-chemical properties of surfaces of plasma polymer films. In many cases, however, it is also desirable to probe the internal structure of both modified and unmodified plasma polymer coatings in order to optimise their properties for a given application.. Reflectometry techniques are now becoming increasingly important in the characterization of nano-scale structured interfaces. X-ray reflectivity in particular is ideally suited to the study of the internal properties of layered film structures on surfaces, yielding data concerning sub surface structure and material properties. Neutron reflectivity meanwhile offers the ability to characterise surface layers in aqueous environments. In this study heptylamine and allylamine plasma polymer coatings were prepared on silicon wafers, and analysed using X-ray reflectometry before and after further surface modification procedures (e.g. adsorption of protein species from solution). Surface chemistry of the coatings was characterised using X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was also used to characterise both roughness and local film thickness at step-edges on the films. The excellent reflectivity data obtained demonstrate the suitability of plasma polymers for reflectivity studies (primarily due to their low surface roughness). Preliminary experiments on plasma polymer layers using neutron reflectivity are also described, which highlight the effect of surface hydration on layer properties.

8:40am **PS+BI-FrM2 Angle Resolved XPS Characterisation of Plasma Polymerised Chemical Gradients***, K.L. Parry,* Plasso Technology Ltd.*; A.G. Shard,* University of Sheffield, United Kingdom, UK*; R.G. White,* Thermo Electron Corporation, UK*; J.D. Whittle,* Plasso Technology Ltd.*; **A. Wright**,* Thermo Electron Corporation, United Kingdom, UK

Well-defined chemical gradients are potentially important materials in a wide range of research activities. The surfaces of such materials can be derivatised with differing functional groups to provide spatially resolved surface chemical properties. Such surfaces can, for example, be used to immobilise biomolecules, which may become a route to producing novel biosensors. This study is concerned with chemical gradients within thin layers of plasma co-polymers deposited onto glass substrates. Continuous gradients of chemistry (hydrocarbon to either acid or amine) are produced by carefully programming the composition of the plasma monomer mixture while varying the area of the substrate exposed to the plasma. It will be shown that spatially resolved XPS is an ideal tool to determine the composition of the near surface region as a function of distance along the chemical gradient. Parallel angle resolved XPS provides additional information about the uniformity of the layer with depth. Such measurements can show, for example, surface enrichment of one of the functional groups in the co-polymer layer or variations in thickness along the chemical gradient. It is therefore possible to construct chemical state and thickness line scans or maps from the same ARXPS data set. Such data provide valuable information regarding the plasma co-polymer deposition process.

9:00am **PS+BI-FrM3 Surface Characterization of Plasma Processed Bio-Functional Micro-Patterned Polymeric Surfaces***, **A. Valsesia**, M. Manso, M. Kormunda, P. Colpo, D. Gilliland, G. Ceccone, F. Rossi,* EU-JRC-IHCP, Italy

The functionalization of the material surfaces is one of the major requirements for the control of the biological response and for the improvement of the biocompatibility. Among the functionalization techniques, PE-CVD is of high importance since the control of the film properties is achieved by an accurate modulation of the plasma processing parameters. PE-CVD allows the synthesis of a wide spectrum of bio-functional polymers: acid/base fouling surfaces (PAA, PAL) and super-hydrophilic anti-fouling surfaces (PEG, PEG-like coatings). Moreover the combination of plasma deposition and plasma etching techniques allows the formation of micro and nano-patterned surfaces with contrasted functionalities. In this work we have studied the plasma deposition of PAA (COOH functional), PAL (NH2 functional) and PEG-like (anti-fouling) layers. The chemical surface characterization of the films has been performed by XPS and TOF-SIMS and the surface free energies components have been calculated by Contact Angle in static and dynamic mode. QCM provided the evaluation of the mechanical stability of the samples in buffer solutions as well as the calculation of the bio-activity of the surfaces in proteins absorption experiments. The surface topography of the samples has been investigated by AFM. The micro-patterned surfaces have been characterized by TOF-SIMS and XPS in imaging mode, revealing the capability of the plasma processing techniques to produce chemically contrasted micrometric motives. The bio-response (protein absorption and cell adhesion) of the micro-patterned samples is under study.

9:20am **PS+BI-FrM4 Plasma Sterilisation and De-pyrogenation of Surfaces: Review and Analysis of Mechanisms***, F. Rossi, R. De Mitri, M. Hasiwa,* European Commission Joint Research Centre, Italy*; S. Bobin, R. Eloy,* Biomatech, France*; T. Hartung,* European Commission Joint Research Centre, Italy*; **P. Colpo**,* EU-JRC-IHCP, Italy

Mechanisms of plasma sterilisation are reviewed and analysed in terms of radiation induced desorption, UV radiation effects and etching. Different plasma discharges are analysed with Optical Emission Spectroscopy in order to find optimum conditions of UV emission and radicals production. Those effects are compared and related to effective sterilisation and depyrogenation rates obtained from the literature and experimentally on Bacillus subtilis and LPS. It is shown that UV emission is the major contribution for sterilisation and chemical etching for depyrogenation. SEM analysis of spores at different times of treatment show the degradation of the outer shell, as well as size and coverage reduction as the treatment duration increases. Effects of plasma on pyrogen is illustrated by AFM and ToF SIMS. A strategy for optimised sterilisation and depyrogenation treatment is proposed.

9:40am **PS+BI-FrM5 Plasma Processes for Micro- and Nano-Patterning Biomedical Polymers***, **P. Favia**,* University of Bari, Italy **INVITED**

Low pressure plasma processes can tune chemical composition, surface energy and topography of most substrates of biomedical interest in a well controlled way. Among the wide range of plasma-modification procedures, micro- and nano-patterning plasma-deposition processes of thin coatings are among the most interesting and novel technologies aimed to drive the behaviour of cells on surfaces. Two kind of plasma procedures will be described in this contribution, and some interesting in vitro tests will be discussed. The first one consists in the deposition of "cell-repulsive" coatings through physical masks to produce patterned surfaces; here "cell-adhesive" domains are alternated to non-adhesive ones. The second process involves the deposition of teflon-like coatings of CF@sub x@ chemical composition, including randomly distributed surface features with nanometric dimensions, which are peculiar of certain deposition conditions in modulated regime. Acknowledgments This research has been developed in the framework of the MIUR-FIRB RBNE01458S_006, COFIN '99 "Biomaterials with micro- and nano- structured surfaces" and 'NANOMED' QLKE-CT-2000 projects, whose financial contribution is gratefully acknowledged.

10:20am **PS+BI-FrM7 Novel Plasma Modification of Microfluidic Devices for Control of Electroosmotic Flow***, **E.R. Fisher**, C.S. Henry, M.A. Boggs, I.T. Martin, Y. Liu, C.D. Garcia,* Colorado State University

Microchip capillary electrophoresis (CE) is a widely used separation technique that combines the efficiency of CE with the portability of a microchip. Poly(dimethylsiloxane), PDMS, is often used to fabricate these microfluidic devices because it is inexpensive, has good optical properties, and the fabrication of complicated channel geometries is straightforward. Separations that occur in PDMS are based on the electroosmotic flow (EOF) within the channel. This, in turn, depends on the density of negatively charged groups on the PDMS surface, which is sensitive to both the pH of the solution and the sealing method (air plasma treatment, methanol). An additional issue is the hydrophobicity of the PDMS, which leads to the adsorption of hydrophobic analytes such as proteins during separations. The goal of this work is to treat PDMS with both non-depositing and depositing plasmas and fully characterize the altered surface chemistry, and its effects on EOF and separations. We have used depositing plasma systems to alter preassembled PDMS microchips, yielding novel surface chemistries. Plasma treated PDMS has been characterized using various surface analysis techniques, including contact angle measurements and

XPS. XPS mapping shows that fluorocarbon (FC) plasma treatments permeate the channel via the reservoirs, not through the porous PDMS. Consequently, the reservoirs and channel are selectively coated with a FC film, resulting in reduced EOF. Conversely, plasma deposition of a hydrophilic hydrocarbon film yielded an increase in EOF. Selected coatings are stable over multiple EOF measurements. Separations conducted with treated chips evaluate biomolecule fouling characteristics. This is the first report of the modification of these devices via depositing plasma systems; plasma treatment of PDMS microchips has essentially been limited to O_2 or air plasmas to oxidize or cure the PDMS, for the enhancement of adhesion of PDMS to PDMS/glass.

10:40am **PS+BI-FrM8 Thiol-Based Plasma Polymer Coatings as Platforms for Biosciences Applications**, ***P.G. Hartley**, S.K. Øiseth, T.R. Gengenbach, G. Johnson, K.M. McLean,* CSIRO Molecular Science, Australia

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, for example, to enhance biocompatibility or to introduce defined chemical functionalities at interfaces for the subsequent coupling of bioactive molecules have seen their widespread application in the field of biomaterials research. We report on the development of sulphur containing plasma polymers using ethanethiol as the feed monomer. In order to ascertain the influence of deposition conditions on the properties of the films, a range of protocols were employed. The films were characterised by X-ray photoelectron spectroscopy (XPS); atomic force microscopy; streaming potential and contact angle measurements. Since XPS data are not sufficiently specific to distinguish between similar carbon-sulphur functional groups (e.g. thiol vs. sulphides), the nature and density of the surface functionalities were quantified by using a thiol specific maleimide containing probe. The stability of the films was tested by assessing coating thickness and chemistry before and after autoclaving. The effects of ageing in air, particularly with respect to the chemical structure were monitored over several months. The incorporation of sulphur functionalities provide reproducible supports for the subsequent grafting of proteins and for the adhesion of gold nanoparticles. The coatings were also shown to act as supporters of cell attachment and growth.

11:00am **PS+BI-FrM9 The Low Damage Surface Modification of the Self-assembled monolayer by the N_2 Neutral Beam Irradiation**, ***Y. Ishikawa**,* Tohoku University, Japan; *T. Ishida,* National institute of Advanced Industrial Science and Technology, Japan; *S. Samukawa,* Tohoku University, Japan

For the realization of future organic molecular devices, controlling surface property of molecular film, such as the electric properties of organic molecule, is quite important. To improve surface property of molecular film, fine surface modification method is highly expected. Thus, we propose the method for controlling the surface properties of organic films by applying plasma process. For this purpose, we used our nearly developed the neutral beam system.[1] The system could prevent the charged particles and ultraviolet photons, and only the neutral particles were irradiated to the substrates. In this study, we irradiated the N_2 neutral beam to the robust self-assembled monolayers (SAMs) made from terphenyls[2] on the gold substrate as the first attempt for neutral beam system to the organic molecular thin films. Energy of the N_2 neutral beams are at the highest 10 eV. We compared the X-ray photoelectron spectra of terphenyl SAMs before and after the N_2 beam irradiation. Then the C-N bonds were generated by the beam irradiation with maintaining the surfer molecular structure. This result indicates that the surface of the terphenyl SAMs would be replaced from carbon or hydrogen to nitrogen, and we can expect that the electric properties of the organic materials would be drastically changed by this method.

[1] S. Samukawa, K. Sakamoto, and K. Ichki: Jpn. J. Appl. Phys., Part 2 40, L779 (2001)
[2] T. Ishida, M. Sano, H. Fukushima, M. Ishida, and S. Sasaki: Langmuir, 18, 10496 (2002).

Plasma Science and Technology
Room 213A - Session PS1+DI-FrM
High K and Difficult Materials Etch

Moderator: A. Miller, LAM Research

8:20am **PS1+DI-FrM1 Inductively Coupled Plasma Etching of Poly-SiC in SF6 Chemistries**, ***S.H. Kuah**, P.C. Wood,* SAMCO International Inc.

A study was made to find a low cost and robust etching solution for silicon carbide (SiC) using a commercially available inductively coupled plasma etching tool. Sulfur hexafluoride (SF6) was selected because of its high degree of F dissociation and non-hazardous nature. A parametric study of the etching characteristics of poly-SiC in inductively coupled plasma (ICP) SF6 chemistries was performed. Etch chemistry was found to greatly affect etch rate, selectivity, final surface cleanliness and smoothness. Etch rates as high as 5884 Å/min were achieved with high SiC/Cr selectivity (36) and clean, but relatively rough etched surfaces (134 Å RA) using a SF6/CF4/He gas mixture. It was found that He addition apparently increases the ionization of SF6 in the plasma and thus increases the SiC etch rate due to increases in the SF3+ and F radical concentrations[1,2]. The formation of pillar-like structures and side wall deposition was observed on the etched SiC surfaces under some conditions. These unwanted etch by-products exhibited a high concentration of Cr and Fluorine. However, an Ar plasma pre-clean of the the substrate, or high ICP and/or bias powers, and CF4 addition can reduce the pillars formation significantly.

[1] J.D.Scofield, B.N.Ganguly, and P.Bletzinger, J.Vac.Sci.Technol. A 18, 2175 (2000).
[2] Z.A.Talib and M.Saporoschenko, Int. J. Mass Spectrom. Ion Processes 116, 1(1992).

8:40am **PS1+DI-FrM2 A Study of Inductively Coupled Plasma Etch of GaN/InGaN Based Light Emitting Diodes**, ***H.D. Chiang**, K.C. Leou,* National Tsing Hua University, Taiwan, ROC; *C.H. Shen, S. Gwo,* National Tsing Hua University, Taiwan; *M.H. Wu,* Uni Light Technology Inc., Taiwan; *C.H. Tsai,* National Tsing Hua University, Taiwan

Group III-Nitride semiconductors are of considerable interest because of their potential for optoelectronic applications such as light-emitting diodes (LEDs) and laser diodes (LDs) in the visible light regions. The dry etching process is one of the critical steps in the fabrication of nitride-based LEDs. A study based on Taguchi experimental design was carried out to investigate the etch characteristics of GaN/InGaN quantum well light emitting diodes using a high density inductively coupled plasma of BCl_3/Cl_2-based chemistry. The process parameters studied include inductive power, bias power, BCl_3/Cl_2 gas ratio and chamber pressure. The etch characteristics measured were etch rate, surface roughness, side-wall angle and etch selectivity to SiO_2 mask. It was found that the variations in the bias power had maximum effect on the etch rate whereas the pressure affected etch rate the least. Anisotropic profiles were generally achieved over a wide range of parameters with low substrate bias. Certain interesting phenomena such as grass and sidewall striations were observed. Nearly smooth etched surface were observed for most etch conditions. The etch mechanisms of different etch conditions on both GaN grown by MBE and MOCVD and the differences of surface roughness before and after etching will also be discussed.

9:00am **PS1+DI-FrM3 High-k Materials Etching**, ***D. Wu**, B. Ji, S.A. Motika, E.J. Karwacki, M.J. Plishka,* Air Products and Chemicals, Inc.

As integrated circuit (IC) device geometry shrinks, high-k materials are needed to maintain adequate breakdown voltage. Due to their high chemical inertness and extremely low volatility, removal of the high-k materials has been technically challenging. In this paper, we will present an effective plasma etching process where a mixture of BCl3 and NF3 is identified as the reactive gas. Compared to pure BCl3, the etch rate for HfO2 was doubled after adding 25% NF3 to BCl3, and the etch rate for HfSixOy was also doubled after adding 15% NF3 to BCl3. Pure BCl3 did not etch ZrO2 at a condition of 0.55 W/cm2 power density and 500 mTorr chamber pressure. But an etch rate of 6 nm/min was achieved when using a mixture of 20% NF3 in BCl3. Detailed experimental setup and data analysis will be reviewed in this paper.

9:20am **PS1+DI-FrM4 Ion-Enhanced Plasma Etching of Metal Oxides in Chlorine Based Plasmas**, ***D. Ramirez**, Y. Ta, 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-90nm 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@ 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, Hf@sub 1-x@Al@sub x@O@sub y@. The dominant etch products of Al and Hf metals in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides. However, the dominant etch products of Al@sub 2@O@sub 3@ and HfO@sub 2@ in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides and metal boron-oxy-chlorides, respectively. These results allowed us to assess 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. Enhanced surface chlorination of the metal oxide surfaces was observed with increasing ion energy, which demonstrates that the etching reaction is limited by the momentum transfer from the ions to the film surface. The etch rates of Al@sub 2@O@sub 3@ and HfO@sub 2@ and their selectivities to Si were found to increase in BCl@sub 3@ plasmas due to the increased oxygen removal rate. Etching of Hf@sub 1-x@Al@sub x@O@sub y@ will also be presented, with a focus on predicting its etch rate based on the etching of Al@sub 2@O@sub 3@ 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 Al@sub 2@O@sub 3@ and Hf@sub 1-x@Al@sub x@O@sub y@ in chlorine based plasmas will be discussed.

9:40am **PS1+DI-FrM5 Investigation of Etching Properties of HfSiO and HfSiON as Gate Dielectrics*, J.H. Chen*,** *W.S. Hwang,* National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; S.H.D. Chan,* National University of Singapore

Hf based high-K dielectrics have been studied as the alternative gate dielectric. For the high performance logic device application, HfSiON is receiving significant attention as the most promising dielectric material because of its good thermal stability, immunity to boron penetration and high carrier mobility in the channel under the gate. In advanced HfSiON films, N profile is optimized: the top HfSiON is highly nitrided to block boron penetration, but the bottom near Si substrate remains as HfSiO to maintain high carrier mobility in the channel. We investigated the etching properties of Hf@sub x@Si@sub 1-x@O@sub 2@ (x=0, 0.3, 0.5, 0.7 and 1) and their nitrided films in ICP of Cl@sub 2@/HBr/O@sub 2@. Results show that etch rates of HfSiO and HfSiON increase rapidly with increasing ion energy, ion density and ratio of Cl@sub 2@. Linear dependency of etch rates on the @sr@E@sub ion@, which obeys the universal energy dependency model of ion enhanced chemical etching yields, was observed with the etch threshold energies of 30-36 eV for HfSiO with different Si% in Cl@sub 2@/HBr. Etch rates of HfSiO and HfSiON are strongly dependent on the open area of the wafer because the oxygen released from these films can suppress the etching process. The addition of the small amount of O@sub 2@ to Cl@sub 2@/HBr plasma or increasing pressure can suppress the etching of HfSiO and HfSiON effectively. The 6nm thick HfSiO or HfSiON can be removed by a wet chemical of 1% HF (DHF) in 30s before anneal; after 700@super o@C anneal, etch rates drop slightly but the densified HfSiO interfacial layer (IL) of ~1nm cannot be removed in DHF. By incorporating N by the plasma nitridation, this IL can be removed by DHF in 10s, and very little Si substrate recess and clean surface can be achieved. This combined approach of the plasma etching and the wet removal proved that HfSiON can be integrated into advanced CMOS processes successfully.

10:00am **PS1+DI-FrM6 Etching of HfO@sub 2@ and HfSiO@sub x@ at Elevated Temperatures*, M. Hélot,*** CNRS, France*; G. Borvon, T. Chevolleau, L. Vallier, O. Joubert,* LTM-CNRS, France*; P. Mangiagalli, J. Jin, Y.D. Du, M. Shen,* Applied Materials

In CMOS technology, the traditional SiO@sub 2@ used as gate dielectric is being replaced by a material presenting a higher dielectric constant (so called high-K materials) for the 65 or more likely the 45 nm nodes. In the integration of such materials, the etch process is one of key issues since the volatility of etch by-products is low and the high-K/Si selectivity seems extremely difficult to achieve. This work is dedicated to the etching of HfO@sub 2@ and HfSiO@sub x@, two of the most promising candidates, using an industrial inductively coupled plasma source (ICP) with a hot cathode (the temperature range of the wafer can be adjusted from 200 to 350°C). Vertical high-K profile without footing or silicon recessing have been achieved. AFM measurements of silicon surface show an acceptable substrate roughness after etch. The etch process has to be adjusted with respect to the deposition technique (CVD vs. ALD) as well the thickness of the silicon oxide buffer layer between the silicon substrate and the high-K layer. XPS analyses reveal that the selectivity is obtained thanks to the formation of a thick C and Cl overlayer on SiO@sub 2@ and not on HfO@sub 2@. Even for these very thin layers, the endpoint techniques such as emission spectroscopy and spectroscopic ellipsometry have to used. Finally we found that the etch process (etch rate and uniformity) depends on the walls reactor seasoning.

10:20am **PS1+DI-FrM7 Ion-enhanced Etching of HfO@sub2@ with Cl@super+@, BCl@subx@@super+@(X = 1, 2) and SiCl @subx@@super+@(X = 1, 2,3) Ion*, K. Karahashi,*** MIRAI-ASET, JAPAN*; N. Mise,* MIRAI-ASET, Japan*; T. Horikawa,* MIRAI-ASRC/AIST, Japan*; A. Toriumi,* MIRAI-ASRC/AIST, Univ. of Tokyo, Japan

As advanced high-k gate dielectrics are being developed to replace SiO@sub2@ in the near future generation of microelectronics devices, understanding their plasma etch characteristics becomes vital for introducing new materials into the manufacturing process. We report on the interactions of HfO@sub2@ with ionic species contained in plasma etching environments. To clarify the ion induced reactions of Cl@super+@, BCl@subx@@super+@(X = 1, 2) and SiCl@subx@@super+@ (X = 1, 2,3), we employed the mass-analyzed ion beam apparatus that can irradiate a single ionic species to the sample surface under an ultra-high vacuum condition. Etching yield of SiCl@sub3@@super+@ ion is about 2 times larger than that of Cl@super+@ ion, and etching products are hafnium chlorides and oxygen atom. This result suggests that chlorine atoms play a key role in etching reaction, and that the chemical etching yield increases with increasing number of chlorine atoms contained in the incident ions. The kinetic energy of etching products, which were estimated by the time delay of etching products with respects to the incident ion pulses, was larger than 0.1 eV. Therefore, products are different from thermally desorbed molecules. This indicates that desorption is caused by the momentum transfer to hafnium chloride. This work was supported by NEDO.

10:40am **PS1+DI-FrM8 Evaluation of the Effectiveness of H@sub 2@ Plasmas in Removing Boron from Si After Etching of HfO@sub 2@ Films in BCl@sub 3@ Plasmas*, C. Wang,*** *V.M. Donnelly,* University of Houston

Etching of high dielectric constant ("high-K") materials in BCl@sub 3@-containing plasmas is challenging due in part to boron residue that deposits on the underlying Si or SiO@sub 2@ surface during the over-etching period. Boron is a p-type dopant and therefore it is best if it is removed prior to subsequent processing. We have investigated the effectiveness of H@sub 2@ plasmas in removing this boron-containing layer. Following etching of HfO@sub 2@ or Al@sub 2@O@sub 3@ thin films in a high-density BCl@sub 3@ plasma, including a 60s overetch period, samples were transferred under vacuum to a UHV chamber equipped with x-ray photoelectron spectroscopy (XPS). After observing B-coverages of ~1 x 10@super 15@ (equivalent of ~ 1 monolayer), the samples were transferred back to the plasma reactor for exposure to the H@sub 2@ cleaning plasma, and then re-examined by XPS. Optical emission spectroscopy was used to monitor B deposition on and removal from the plasma chamber walls. B deposition on the reactor walls during BCl@sub 3@ plasma exposure reached saturated coverage in ~2 min. Following this, the H@sub 2@ plasma removed half of this B layer in 90s, and 90 % in 320 s. B was rapidly removed (< 5s) from the BCl@sub 3@-over-etched Si surfaces provided that the walls were first cleaned in the H@sub 2@ plasma, with the Si sample held in the UHV chamber during the chamber cleaning process. Conversely, it took much longer (~170s) to remove all detectable B on the sample surface if the sample and the reactor chamber walls were cleaned in the H@sub 2@ plasma at the same time. Etching rates of SiO@sub 2@ and Si in the H@sub 2@ cleaning plasma will be reported. Mechanisms of B deposition on and removal from chamber walls and Si and SiO@sub 2@ surfaces will be discussed. A less effective sequential O@sub 2@/H@sub 2@ plasma cleaning process will also be presented. Supported by SRC and AMD Inc.

11:00am **PS1+DI-FrM9 Selective Etching of HfO@sub 2@ High-k Dielectric over Si in C@sub 4@F@sub 8@/Ar/H@sub 2@ Inductively Coupled Plasmas*, K. Takahashi*,** *K. Ono, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. Regarding gate dielectrics, the technological challenge continues for growing ultrathin SiO@sub 2@ films of high quality; however, the ultimate solution relies on high dielectric constant (k) materials. In integrating high-k materials into device fabrication, an understanding of the etching characteristics of the materials is required for their removal

and for contact etching. This paper presents the etch rates and possible etch mechanisms for HfO@sub 2@ thin films on Si substrate in inductively coupled plasmas containing mixtures of CF@sub 4@/Ar/H@sub 2@ and C@sub 4@F@sub 8@/Ar/H@sub 2@, as a function of gas composition and rf bias power. In the experiments, the discharge was established at a gas pressure of 20 mTorr and an rf source power of 280 W. The gas flow rates of fluorocarbon and Ar were 2.5 and 247.5 sccm (the ratio of fluorocarbon to total was 1 %). The rate of H@sub 2@ was varied between 0 and 16 sccm. As the dc selfbias voltage was maintained at the constant value of -90 V, HfO@sub 2@ and Si were etched in the CF@sub 4@/Ar/H@sub 2@ plasma with no relation to H@sub 2@ flow rate. In the C@sub 4@F@sub 8@/Ar/H@sub 2@ plasma, however, the conditions could be found where HfO@sub 2@ was etched at the rate more than 10 nm/min, and the fluorocarbon polymer deposited on Si. In this regime, it can be possible to selectively etch HfO@sub 2@ over Si. The chemical composition of the polymer was carbon-rich, and the carbon content on HfO@sub 2@ was not so much as on the polymer. It can be said that carbonized products may correspond to etch products for HfO@sub 2@. @FootnoteText@ This work was supported by NEDO/MIRAI Project.

11:20am **PS1+DI-FrM10 Characterization of the Sputtering Process in an rf Plasma for the Patterning of Nonvolatile Materials***, **T.J. Kropewnicki**, A.M. Paterson, T. Panagopoulos, J.P. Holland,* Applied Materials, Inc.

With the integration of nonvolatile materials into microelectronic devices, such as NiFe in magnetic random access memory, perovskites in ferroelectric random access memory, and HfO@sub 2@ as a transistor gate dielectric, it has become necessary to develop methods of characterizing the patterning of these materials. Removal of these nonvolatile materials by sputtering with heavy ions is probably a key component of the etching mechanism. Sputtering of materials by ion bombardment has typically been characterized using high energy ion beam systems, leading to sputtering yield probabilities as a function of ion energy. Since typical commercial plasma etch reactors use rf power to energize the ion bombardment, the usefulness of these sputtering probabilities in understanding the reaction mechanism is limited by the much lower energy levels being produced by the rf sheath, and by the spread of ion bombardment energies typically produced by an rf plasma sheath. Ion energies less than 1000 eV are common in many plasma etch systems. To create a more realistic picture of the etching process, direct measurements of the actual rf waveforms occurring on the wafer are transformed using a simple plasma sheath model into ion energy distribution functions which are then used in combination with the reported sputtering yield data to predict more accurate sputter yields for these conditions. Langmuir probe measurements of ion fluxes are then used to determine the etch rates. Comparison of these predicted rates and actual measured rates will be presented as well as possible reasons for discrepancies between the two rates.

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