Monday Morning, November 13, 2006

Plasma Science and Technology
Room 2009 - Session PS1-MoM

Etch for Advanced Interconnect I
Moderator: L. Stafford, University of Florida

8:00am **PS1-MoM1 Fluorocarbon-based Plasma Etching Processes for Silicon Dioxide and Silica Dielectrics - Mechanistic Insights and Current Issues*, G.S. Oehrlein*[1]**, University of Maryland **INVITED**
Plasma-based transfer of resist patterns into silica-based dielectric materials using fluorocarbon discharges is one of the most widely employed and investigated application of plasma etching processes. Despite its long history and intensive research and development efforts, a number of important questions remain in our understanding of silicon dioxide plasma etching processes. In addition, the transition to lower dielectric constant insulators in back-end-of-line structures is based on an evolution from silicon dioxide to silica containing carbon-groups and nanopores. With this conversion, certain aspects of the plasma etching processes change and new phenomena can become important. In this talk we present an overview of important developments and current issues in this field.

8:40am **PS1-MoM3 Effect of Species Density and Ion Bombardment during Ashing of Extreme Ultra Low-@kappa@ (eULK) Inter-Level-Dielectric (ILD) Materials*, M.A. Worsley,*** Stanford University*; N.C.M. Fuller,* IBM Research Division*; S.F. Bent,* Stanford University*; T. Dalton,* IBM Research Division
The significance of ion impact and radical species density on ash-induced modification of an extreme ultra low-@kappa@ (eULK) inter-level dielectric (ILD) material (@kappa@ < 2.0) in a patterned single damascene structure exposed to Ar/O@sub 2@ and Ar/N@sub 2@ dual frequency capacitive discharges is determined by combining plasma diagnostics, modeling of the ion angular distribution function (IADF), and material characterization such as angle resolved x-ray photoelectron spectroscopy (ARXPS). Radical species density was determined by optical emission (OE) actinometry under the same conditions and in the same reactor in a previous study by the present authors. ILD modification is observed and correlated with changes in the plasma for a range of pressures (5-60 mTorr), bias powers (0-350W), and Ar in the source gas (0%, 85%). For the Ar/O@sub 2@ discharge, extensive modification of the ILD sidewall was observed for significant ion scattering conditions and vice versa. Further, for an identical increase in the O-radical density (~ an order of magnitude) as pressure or percent Ar was increased, a different degree of modification was induced at the ILD trench bottom surface and seemingly correlated with the relative changes in the ion current for increasing pressure or percent Ar. For the Ar/N@sub 2@ discharge, reduced damage of the ILD sidewall and trench bottom surfaces was observed for increasing pressure (increasing N-radical density) and decreasing ion current to both surfaces. It is, thus, proposed that the mechanism for modification of the porous ILD is dominated by the creation of reactive sites by ion impact under the present conditions. A detailed discussion of the results in relation to this proposal is presented.

9:00am **PS1-MoM4 Systematical Evaluation of Etching Damage of Light, Radicals and Ions on Low-k Porous SiOCH Films*, S. Takashima,*** *S. Uchida, M. Hori,* Nagoya University, Japan*; K. Oshima, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan
In order to reduce the RC delay of ULSIs, insulating materials with lower dielectric constant (low-k) are introduced. The low-k films receive the damages from the plasmas in the etching and ashing processes. The plasma damages induce the increase of the dielectric constant of the films. In this study, we have investigated the etching damages of the low-k films by the process plasmas and clarified the influences of light, radicals, and ions in the plasmas on the properties of the low-k films systematically. The low-k film used in this study was the porous SiOCH film. In order to separate the influence of light, radicals and ions, we have developed a new technique, where the four kinds of etching samples were prepared. The MgF@sub 2@ and quartz window were put directly on the film, respectively, to clarify the influence of vacuum ultraviolet (VUV) light and UV light from the plasmas. The MgF@sub 2@ and quartz windows transmit the light of wavelength 115nm or more and 170nm or more, respectively. Si plate was put 0.7 mm above the film surface to investigate the influence of radicals. In order to clarify all the influences of light, radicals and ions, nothing was put on the film. The dual frequency CCP apparatus of 8 inch wafer was used. The refractive index and the film thickness were measured by an ellipsometer. At a VHF power of 500W, a bias power of 500W, a gas flow rate ratio H@sub 2@/(H@sub 2@+N@sub 2@) of 50%, and a pressure of 5.3 Pa, the increase of the refractive index was caused by not only the radicals and the ions but also the VUV and UV lights from the plasmas. On the basis of results, degree of the damages induced by individual species and light have been clarified.

9:20am **PS1-MoM5 Negative Ions in Dual-Frequency Capacitively Coupled Fluorocarbon Plasmas*, G.A. Curley*[2]**, Ecole Polytechnique, France*; J.P. Booth,* Lam Research Corporation*; D. Mari@aa c@,* Ecole Polytechnique, France*; C.S. Corr,* Australian National University*; J. Guillon,* Ecole Polytechnique, France
Dual-frequency capacitively coupled plasmas in fluorocarbon-based gases are widely used for etching contact holes in SiO@sub 2@-based dielectric films in integrated circuit manufacture. We are studying a customized 2 + 27 MHz industrial etch reactor, running in Ar/O@sub 2@ with c-C@sub 4@F@sub 8@ or CF@sub 4@ gas mixtures at pressures in the region of 50 mTorr (6.6 Pa). Negative ions could play an important role in this type of plasma. The presence of negative ions will modify the positive ion flux arriving at a surface, and may even reach the surface and participate in etching. We have measured the electron density using a microwave hairpin resonator@footnote 1@ and the positive ion flux with an ion flux probe:@footnote 2@ the ratio of these two quantities varies strongly with gas chemistry and gives evidence for the presence of negative ions.@footnote 3@ For example, by varying the flow of c-C@sub 4@F@sub 8@ in an Ar/O@sub 2@ mixture this ratio shows evidence of high electronegativity for high c-C@sub 4@F@sub 8@ flowrates. We have also measured the negative fluorine ion, F@super -@, density directly by high-sensitivity cavity ring-down absorption spectroscopy@footnote 4@ in the wavelength range 340 to 360 nm to determine the density of absorbing F@super -@ ions from the known photo-detachment cross-section. The F@super -@ densities were seen to reach values in the 10@super 11@cm@super -3@ range, giving electronegative fractions, @alpha@ = n@sub -@/n@sub e@ of up to 15 when used in conjunction with the hairpin probe measurements. We acknowledge financial assistance from Lam Research Corporation. @FootnoteText@ @footnote 1@ Piejak et al, J. Appl. Phys. 95 (2004), 3785-3791@footnote 2@ Braithwaite et al, Plasma Sources Sci. Technol., 5 (1996), 677-684@footnote 3@ Chabert et al, Plasma Sources Sci. Technol., 8 (1999), 561-566@footnote 4@ Booth et al, Appl. Phys. Lett., 88 (2006), 151502.

9:40am **PS1-MoM6 Plasma and Etching Characteristics for C@sub 6@F@sub 6@ Gas*, S.C. Park*,** *H.S. Shin, J.W. Sun, C. Shin, C.-J. Kang, H. Cho, J.-T. Moon,* Samsung Electronics, Korea*; M.S. Kim, B. Ji, W.J. Howard,* Air Products and Chemicals, Inc.
In this paper for studying plasma and etching characteristics of C@sub 6@F@sub 6@, we chose C@sub 6@F@sub 6@ as one of the promising candidates of next generation high aspect-ratio contact(HARC) etching gas because it could make more polymer than C@sub 4@F@sub 8@ and C@sub 4@F@sub 6@ which widely used as HARC etching gas. High polymer generation characteristic could resolve the selectivity problem which has become more serious in sub-100nm HARC etching. To identify the difference between C@sub 6@F@sub 6@ and other gases, plasma and etching characteristics were compared. Quadrupole mass spectroscopy(QMS) and optical emission spectroscopy(OES) were used to identify plasma characteristics and X-ray photoelectron spectroscopy(XPS) was used to investigate the polymer from each gases. Gases were used for sub-100nm HARC etching and etching characteristics were compared. Commercial CCP-type etcher was used for etching. C@sub 6@F@sub 6@ showed 1.7 times higher polymer deposition rate than C@sub 4@F@sub 8@, but it showed lower C/F ratio in polymer than other gases contrary to higher C/F ratio in the gas. This C/F ratio in polymer affected profile and selectivity during HARC etching. From QMS study, we knew that C@sub 6@F@sub 6@ cracked into relatively larger molecules than other gases at the same condition, and CF@sub 2@@super +@ ion was not observed from C@sub 6@F@sub 6@ cracking patterns as we could expect from C@sub 6@F@sub 6@ gas structure. This fragment patterns also affected polymer composition and etching characteristics. We used C@sub 6@F@sub 6@ to etch sub-100nm HARC etching and compared with other gases.

[1] **2005 Plasma Prize Winner**

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

10:20am **PS1-MoM8 New Challenges in Etching Ultra Low-k Dielectrics for 45nm and Beyond***, A. Li,* *K. Zhou, Y. Zhou, R. Cheung, S. Parikh, M. Armacost,* Applied Materials, Inc.

Abstract Ultra low-k (ULK) dielectrics with k-values below 2.5 have been extensively evaluated for 45 nm node and beyond. Most ULK dielectrics have highly connected pore structure and therefore, exert new challenges during plasma processing. Conventional O2-based plasma resist stripping processes can cause significant loss of -CH3 groups, surface densification and pore collapse in ULK, and therefore, lead to film shrinking, profile distortion and an increase of its k value. The pore structures can also induce surface roughness and micro trenching. In this paper, physical findings on ULK damage and rough etch front/micro trenching and electrical validations in a high frequency capacitive coupled plasma etch chamber have been reported. Both O- and N- based chemistry have been investigated for in-situ resist stripping and the dependences of damage and etch front on gas flow rates, pressure, rf power and power ratio have been studied. Auger Electron Spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS) have been employed to probe the degree and depth of chemical composition changes in the modified ULK layer. The results suggest that in-situ stripping plays an important role in controlling ULK damage and final ULK etch front. The ULK damage and rough front/micro trenching formation mechanisms have also been discussed.

10:40am **PS1-MoM9 Analysis of Plasma-Induced Modification of Porous SiOCH Low-k Materials during Etching and Post-Etching Plasma Processes***,* ***K. Kurihara****, H. Hayashi, T. Ohiwa,* Toshiba Corporation, Japan

Porous SiOCH low-k materials have been extensively investigated to achieve high performance interconnect for ULSI devices. However, etching damage arising from high porosity and low density becomes serious problems. During the etching process, a large amount of fluorine diffused into the porous low-k film, and carbon was easily removed from the film. This fluorine absorption and carbon loss would deteriorate the low-k property and the low-k/Cu interconnects reliability due to moisture uptake. Therefore, fluorine removal from the film is required. In this paper we examined plasma-induced modifications of the porous SiOCH low-k film by fluorocarbon gas mixture plasmas, and subsequent plasma treatment using by H@sub 2@ gas. In the actual dry etching condition, fluorine atoms were adsorbed to the side walls of etched patterns without ion bombardment, and diffused into the film. To simulate this condition, the blanket low-k samples were irradiated by only neutral reactive species using a plasma beam apparatus.@footnote 1@ After the fluorocarbon radical beam irradiation, the film properties were analyzed by quasi-in situ XPS and SIMS. Fluorine atoms were deeply distributed into the film, and they were hardly eliminated by any plasma irradiation conditions at room temperature. On the other hand, a certain amount of fluorine atoms bonded to carbon were scavenged by the subsequent H@sub 2@ plasma irradiation at higher substrate temperature. After this process we have observed no fluorine signal at TDS measurement where the film was heated up to 800°C. Remained fluorine atoms in the film after this process were bonded to silicon atoms, and it was difficult to desorb from the film. Therefore, it was clearly shown that the post-etching processes using H@sub 2@ plasma at higher temperature were useful to reduce fluorine content in the film, and to achieve higher reliability of low-k/Cu interconnects. @FootnoteText@ @footnote 1@K.Kurihara et al. J. Vac. Sci.Technol. A 22, 2311(2004).

11:00am **PS1-MoM10 Material Modifications and Surface Roughness during Porous SiOCH Etching Processes***,* ***F. Bailly****,* CNRS-IMN-France, France*; T. David,* CEA-LETI-France, France*; A. Jacquier,* STM-France*; M. Darnon,* CNRS-LTM-France, France*; C. Cardinaud,* CNRS-IMN-France

With dimensions shrinkage, chip performances limitations are mainly due to interconnect RC delay time. Introducing porosity into dielectrics, leading to ultra low-k materials, is one of the emerging solutions. Integrating such porous materials requires complex dual damascene architectures: new steps and additional layers (etch stop ...) have been added and increase the effective capacitance of the structure. Efforts have to be done to reduce the effect of these layers. Thus, the trench bottom etch stop layer used in the dual damascene architecture has to be removed, complicating the control of the end of the trench etch. Furthermore, stopping the etch process directly on the porous material is likely to cause integration issues such as material modifications and roughness of the trench bottom. As a basic study, we simulate the influence of etch plasmas on trench bottom. We propose to characterize material modifications and roughness induced by the etch plasmas on blanket wafers coated with porous SiOCH (20% of porosity). These plasmas are performed in a capacitive discharge reactor. The feed gases are chosen to be representative of the different components of a typical low-k etch process (CF@sub 4@; Ar = role of bombardment; SF@sub 6@ = role of fluorine; CF@sub 4@/Ar/CH@sub 2@F@sub 2@ = effect of a polymerizing gas addition; CF@sub 4@/Ar/N@sub 2@; ...). The roughness is measured by AFM and is correlated with surface analyses (XPS and XRR) to point out any relations between etch mechanisms and the resulting roughness. Results highlight that the addition of O@sub 2@ or N@sub 2@ among the feed gases (CF@sub 4@ and Ar) leads to roughness increase. On the contrary, when adding a polymerizing gas, smoother surfaces are observed thanks to a protective fluorocarboned overlayer. The material modification is investigated by Infrared Spectroscopy: the results show that the remaining porous SiOCH is slightly modified in terms of CH@sub 3@ consumption and water uptake.

11:20am **PS1-MoM11 Grain Size Effects on Plasma-based Copper Etch Process***,* ***G. Liu****, Y. Kuo,* Texas A&M University

Copper (Cu) is the most popular interconnect material in advanced VLSIC products because of its low resistivity and high resistance to electromigration. Previously, a novel plasma-based, room-temperature copper etching method was presented.@footnote 1,2,3@ A high etch rate of 400 nm/min has been achieved at room temperature using a conventional reactive ion etching reactor with Cl or Br chemistry. In spite of the thorough understanding of the plasma-Cu reaction process, there is little information on the copper structure effects. In this work, authors investigated the grain size effects on the etching process. Cu films were deposited by sputtering followed by annealing at various temperatures. Several results have been obtained: 1) the grain size and film conductivity increased with the annealing temperature, 2) under the same plasma exposure condition, the Cu consumption rate increased with the grain size, 3) the surface roughness of the CuClx reaction product increased with the grain size, and 4) the Cu line shape and sidewall profile were related to the grain size. In summary, Cu structure is an important factor in the plasma-based etching process and the plasma-copper reaction mechanism dominates the etch rate and the final pattern. @FootnoteText@ @footnote 1@ Y. Kuo and S. Lee, Appl. Phys. Lett., 78, 1002 (2001).@footnote 2@ S. Lee and Y. Kuo, Thin Solid Films, 457, 326 (2004).@footnote 3@ Y. Kuo, Procs. 6th Intl. Conf. Reactive Plasmas and 23rd Symp. Plasma Processing, 29 (2006).

Plasma Science and Technology
Room 2011 - Session PS2-MoM

Advanced Gate Fabrication

Moderator: E.V. Barnat, Sandia National Laboratories

8:00am **PS2-MoM1 Plasma Etch Challenges in Non-Planar Device Fabrication***,* ***U. Shah****, R.B. Turkot, Jr, T. Ghosh, S. Shankar,* Intel Corporation

As transistor development embraces multi-gate devices, new requirements are being placed on the patterning of these new structures. This paper discusses the challenges surrounding plasma etching of non-planar poly silicon gate electrodes required for multi-gate transistor development. The variation in type of structures, underlying materials and aspect ratios will be discussed. Some of the most common problems pertaining to etch processes of traditional planar devices such as gate profiles, notching, charge-induced damage of underlying material and selectivity requirements will be compared and contrasted between planar and non-planar geometries. Simulation results and models of how topography and underlying materials affects gate evolution and methods to control them will also be presented. Current metrology options used to characterize gate patterning and their inherent limitations will also be discussed in this paper.

8:20am **PS2-MoM2 Effect of Photoresist Trimming and Plasma Treatments on Line Roughness, Necking, and Bending During High Density Plasma Polysilicon Gate Etching***,* ***S.A. Vitale****, B.A. Smith, J.W. Blatchford, B.M. Rathsack,* Texas Instruments

Control of the polysilicon gate electrode length during high density plasma etching is one of the most challenging aspects of transistor fabrication at the 45nm technology node. According to the 2005 International Technology Roadmap for Semiconductors, the polysilicon gate length will be as small as 23nm for high performance microprocessors by 2008. Although transistor gate length has been shrinking by approximately 0.7x every 2 years, the line edge roughness has not scaled by the same factor. As a result, line edge roughness now can be as high as 25% of the gate length, resulting in severe degradation of transistor performance. In

addition, systematic variations such as line necking and bending can result in line breakage and ultimately failure of the device. Solutions to reduce polysilicon gate line edge roughness, necking, and bending are critical to enable transistor performance and process yield at the 45nm node. In this work, high frequency line edge roughness of etched polysilicon gates is shown to originate primarily from roughness in the incoming photoresist. Plasma treatment to reduce the gate linewidth, commonly called plasma resist trimming, is shown to reduce the high frequency edge roughness. Line necking and bending, on the other hand, increases during the plasma resist trimming. AFM analysis of photoresist lines shows that torquing stresses during plasma resist trim is a primary factor in polysilicon gate bending and breakage. In general, high frequency line edge roughness is shown to be uncorrelated between the left and right edges of the lines. The effect of resist trimming and plasma treatments on the frequency spectrum of the roughness is also presented. HBr plasma curing, which can be used to harden photoresist and improve selectivity during polysilicon etch, is shown to neither improve nor degrade line edge roughness. Increasing oxygen concentration during the plasma resist trim step can be used to reduce line necking, at a given gate linewidth.

8:40am **PS2-MoM3 Understanding the Impact of Chamber Walls during Plasma Etching: a Key to Control Plasma Processes In ULSI**, ***R. Ramos***[1], Freescale Semiconductor, France; *G. Cunge, O. Joubert,* Laboratoire des Technologies de la Microelectronique, CNRS-LTM, France; *M. Orlowski,* Freescale Semiconductor, France; *T. Lill,* Applied Materials

Decrease in device dimension for integrated circuit manufacturing is challenged by wafer-to-wafer repeatability during plasma etching processes. Today's strategy to minimize potential drifts during plasma processes is to dry-clean the walls of the plasma chamber with an appropriate chemistry between each wafer to efficiently remove the etch products that have been deposited during the etch process. By using a simple technique that can monitor the chamber walls coating (based on X-ray Photoelectron Spectroscopy analyses) we have investigated the deposits formed on the chamber walls after metal / high-k (TiN, TaN, TaC, WSi@sub x@, HfO@sub 2@) gate etching processes, and the associated reactor cleaning strategies. We show that, in the most typical etch and clean processes, chamber walls are inevitably exposed to F-based plasma leading to the formation of AlF@sub x@ residues on the Al@sub 2@O@sub 3@ chamber walls. Sputtering of F atoms and AlF@sub x@ particles from this fluoride layer during the etching process then leads to uncontrolled concentrations of fluorine-based species and metal particles in the plasma gas phase that have an impact on the reliability of the process. We thus have investigated two potential solutions to overcome this issue without changing chamber walls material (for expensive Y@sub 2@O@sub 3@ liners for example): (1) dry-cleaning of AlF@sub x@ residues between each wafer, and (2) protecting the inner parts of the chamber walls with a thin coating before processing any wafer to provide a F-free, reproducible chamber environment. By comparing SiOCl coatings and carbon-rich coatings, we conclude that the latter ensures both better reproducibility and longer chamber walls lifetime, since reactor walls are never exposed to fluorine-based plasmas, therefore preventing AlF formation. Furthermore TEM picture shows that carbon-coated walls exhibit excellent capabilities for advanced gate stack patterning.

9:00am **PS2-MoM4 Effect of Etching Process on Gate LER**, ***A. Yabata,*** *O. Koike, J. Hashimoto, I. Kurachi,* Miyagi Oki Electric Co., Ltd., Japan

In nano-scaled regime of semiconductor devices, effect of gate process on MOSFET is getting large. Especially for etching performance, shrinking technique and stable uniformity length are strictly required. In addition to them, reduction in LER (Line Edge Roughness) is very important too. It is the most critical issue for variability of current status and off stage leakage. Therefore, LER must be reduced for improving MOSFET. In widely study, LER is well known being large in 193nm ArF lithography and has poor durability for etching plasma exposure. But effect of another process parameter is not enough understood yet. In this paper, we focused on gate etching process and gate electrode material,and found new mechanism of gate LER formation.@footnote 1@ LER was evaluated by 3D AFM(Atomic Force Microscope) with sample of PR/BARC/PolySi/Oxide/Si sub. 3D AFM is directly measurement system of sidewall roughness with flared type tip. Firstly, effect of PR/BARC LER on gate LER was evaluated. PR/BARC LER was controlled by changing BARC etching gas chemistry. From the result, gate LER did not change at all without effect of drastic PR/BARC LER change. That indicates gate electrode LER must not be influenced by LER of masking layer. Secondary, the parameter of PolySi gate etching condition was focused. Dependence of pressure, source power, bias power and stage temperature were evaluated. From the result, effective parameter was only bias power and Gate LER was improved with increasing of bias power. That indicates LER has closely related with etching sputtering effect. Finally, we focus on effect of gate electrode material itself. It was was evaluated by surface roughness of PolySi. It was controlled by phosphorus dope method,concentration and anneal condition. From the result, gate LER was closely related with surface roughness. Therefore, gate electrode material is a key factor of LER formation. @FootnoteText@ @footnote 1@A.Yabata,et.al.:ICRP-6/SPP-23(2006) P-2A-30 451.

9:20am **PS2-MoM5 Plasma Atomic Layer Etching Using Conventional Plasma Equipment***, ***A. Agarwal,*** University of Illinois at Urbana-Champaign; *M.J. Kushner,* Iowa State University

The thinning of the dielectric in gate stacks and the need to resolve etching on an atomic layer basis in applications such as FinFETs present large technological challenges in plasma etching. To insure atomic-level control it is desirable to use a self-limiting process which is independent of the processing time. In plasma atomic layer etching (PALE), formation of a monolayer of reactants or passivation is followed by the removal of the layer that then self terminates the process. For example, deposition of a thin layer of polymer or passivation in a non-etching plasma followed by etching in a non-polymerizing plasma with low energy ion energy could remove only a single layer or less of underlying material. The higher threshold energy required to remove the underlying material in the absence of the passivation would self-terminate the process. A challenge is to perform these processes in conventional plasma equipment as opposed to highly specialized beam equipment. In this talk, results from a computational investigation of PALE will be discussed with the goal of demonstrating the potential of the process using conventional etching tools. The Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM) were modified to have pulse periodic capability as required for PALE, and to kinetically resolve ion energy distributions to finely resolve threshold energies. Results for PALE will be discussed, for geometries of interest to future technological nodes, for at least two systems: 1) PALE of Si using steps of an Ar/Cl@sub 2@ plasma (passivation) followed by Ar plasma (etch) and 2) PALE of SiO@sub 2@ using steps of a fluorocarbon plasma (passivation) followed by an Ar plasma (etch). @FootnoteText@ *Work supported by Semiconductor Research Corp. and the National Science Foundation.

9:40am **PS2-MoM6 Impact of Plasma Damage on Cobalt Silicidation**, ***T. Kimura,*** *K. Kugimiya, K. Fuke, T. Ohchi, T. Kataoka, T. Tatsumi, Y. Kamide,* Sony Corporation, Japan

Silicides must be introduced to ULSI circuits to improve sheet and contact resistance. Generally, silicidation on the source and drain depends strongly on the surface, so controlling damage to the silicon substrate from sidewall etching is very important. We studied sidewall etching using a capacitive coupled plasma type etcher. RF power supplies with different frequencies (2 and 13.56 MHz) were used for the lower electrode. The thickness of the damage layer in the silicon surface resulting from sidewall etching was conveniently evaluated by ellipsometry. As Vpp is increasing, the thickness of the damage layer is increasing in the case of sidewall etching with CH@sub 2@F@sub 2@ gas chemistry and the thickness is decreasing in the case of etching with a RF power supply of higher frequency under conditions where the same Vpp was obtained. We calculated the ion energy distribution function. The thickness of the damage layer has a clear relationship to ion energy at the high energy peaks for both frequencies. The damage thickness also depends on gas chemistry. When we used the CF@sub 4@ plasma, the thickness of the damage layer was thinner than that induced by the CH@sub 2@F@sub 2@ plasma and did not seem to depend on RF bias power. This is presumably due to the absence of H ions, which can penetrate Si more deeply. We could successfully form conformal CoSi@sub x@ on the source and drain after sidewall etching with CF@sub 4@ gas chemistry, but we could not after etching with CH@sub 2@F@sub 2@ gas chemistry. For mass production to occur, high quality CoSi@sub x@ must be formed to create 32-nm devices and the control of ion energy distribution in the dry etching system must be improved.

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

10:20am **PS2-MoM8 Plasma Etching Challenges of New Materials Involved in Gate Stack Patterning for sub 45 nm Technological Nodes***, **O. Joubert**,* CNRS-LTM-France, France*; A. Le Gouil,* STM-France*; R. Ramos,* CNRS-LTM-France*; M. Helot,* STM-France*; O. Luere, E. Richard,* CNRS-LTM-France*; G. Cunge, T. Chevolleau,* CNRS-LTM-France, France*; E. Pargon, L. Vallier,* CNRS-LTM-France*; T. Morel,* CEA-LETI-France*; S. Barnola,* CEA-LETI-France, France*; T. Lill, J.P. Holland, A. Patterson,* AMAT-USA **INVITED**

In plasma etching processes, the complexity comes from the introduction of new materials and from the reduction in dimension of the structures involved in CMOS devices. In the gate stack patterning step, the precision of the critical dimension (CD) control required to pattern silicon gates on thin SiON dielectrics has required an unprecedented effort of the etch community to design all the plasma etching steps allowing a CD control better than 3 nm across a 300 mm wafers. The introduction of metal layers and high K dielectric materials in the sub 45 nm gate stack is even more challenging since time and experience are missing to reach the degree of control required to fabricate such complex stacks in a range of dimension between 20-30 nm. In this presentation, we will show what new issues are faced when a metal layer is introduced in the gate stack: etch chemistry compatibility between silicon and metal (strongly metal dependent), profile deformation of the silicon top part of the gate when etching the thin metal layer, process strategy (etch silicon and metal in one step or in two steps), impact of chamber wall coatings on profile control and selectivity issues between metal and high K. The etching of high K HfO@sub 2@ based materials is also complex. First, after metal etching, the thin high K layer has been modified (covered by significant concentrations of halogens, roughness). Furthermore, the thin high K layer must be removed without generating damage in the underlying silicon and without generating profile deformation of the top part of the gate. All the issues will be discussed by showing the practical integration of TiN, TaN, WN, W in advanced gate stacks and discussing our results with the support of powerful in situ characterization techniques such as chemical topography analyses using XPS, mass spectrometry, as well as TEM and SEM cross sections.

11:00am **PS2-MoM10 Ta and Mo-based Metal Etch for Advanced Gate Stacks***, **E. Luckowski**, A. Martinez, S. Rauf,* Freescale Semiconductor, Inc.

The continued scaling of conventional CMOS devices becomes increasing difficult due to the additional series capacitance caused by polysilicon depletion, which decreases gate capacitance and requires increasingly thin gate dielectric layers. High-K dielectrics in conjunction with polysilcon gates address this problem, but interactions between polysilicon and gate dielectric material make implementation of this solution difficult. An increasingly attractive solution to these problems is the use of metal electrodes with suitable work functions and sufficient physical and electrical stability. Because selection appropriate gate electrode is driven mainly by the work function of the metal, these materials pose significant challenges that require an in-depth understanding of plasma etch properties and mechanisms in order to successfully fabricate aggressive dimensions of current advanced gate stack devices. In this work we investigate the impact of plasma parameters on etching characteristics of Ta and Mo-based materials for advanced gate stack device applications. In particular, etch rates and selectivites are discussed with respect to fabricating single and dual metal gate CMOS structures. The impact of metal etch processes on polysilicon and high-k dielectric layers will also be discussed. OES and in-situ reflectometry are used to characterize composition and changes in the plasma conditions, etch rates and profiles measured by four point probe, XRR, SEM and TEM. Plasma modeling is also done using a 2D integrated equipment-feature scale model to improve understanding of the mechanisms of metal gate etch processes.

11:20am **PS2-MoM11 Influence of Stopping Layer Nature on Poly-Si/Metal Gate Patterning Process***, **V. Paraschiv**, D. Shamiryan, M. Demand, S. Beckx,* IMEC, Belgium*; C.G.N. Lee, G. Kota,* LAM Research*; W. Boullart,* IMEC, Belgium

TiN or TaN layers are introduced between poly-Si electrode and the gate dielectric to solve the poly-Si depletion and boron diffusion issues. Although a minimal change is introduced we show that this modification has a significant impact on poly-Si etch due to the nature of the layer underneath the poly-Si electrode (dielectric or metallic). The etch was carried out in a Lam Research Versys2300 etch reactor. Poly-Si gate etch includes main etch (ME), soft landing (SL) and over etch (OE).@footnote 1@ SL is critical since it has to stop on SiO2 and has to keep a straight gate profile. For conventional (poly-Si/SiO2) gate stack the etch time after end point (EP), during SL, defines the bottom profile since the SiO2 starts accumulating positive charges inducing ions deflection at the bottom of the gate.@footnote 2@ The deflected ions remove the poly-Si foot present at the moment of EP. Conventional gate etch could not remove the poly-Si foot when stopping on metal, apparently due to lack of charge accumulation and the corresponding ion deflection. Although, the metallic layer can be oxidized by O2 present in the SL etch chemistry, the bottom power required for ion deflection is too low and results in damaging the top gate profile, due to hard mask charging effect (negatively charged oxide hard mask deflects ions distorting gate profile).@footnote 3@ Changing the ME chemistry from HBr/Cl2/CF4/O2 to SF6/CH2F2/N2 provides better passivation of poly-Si sidewalls allowing a SL step with a very low bottom power (65V) that removes the poly-Si foot without affecting the top profile. Although both TiN and TaN are conductive, it is more difficult to remove the poly-Si foot when stopping on TiN due to their different oxidation behavior. @FootnoteText@ @footnote 1@ E. Pargon et al., J. Vac. Sci. Technol. B 23(5), 1913 (2005).@footnote 2@ G. S. Hwang et al., J. Vac. Sci. Technol. B. 15, 70 (1997).@footnote 3@ D. Shamiryan et al., J. Vac. Sci. Technol. B, 23 2194 (2005).

11:40am **PS2-MoM12 Plasma Etching of Tungsten Nitride for sub 45nm Metal Gate***, **S. Barnola**,* CEA-LETI/France, France*; T. Morel,* STMicroelectronics

With the reduction of the CMOS devices dimensions on standard poly-silicon gates, the poly depletion effect is a major problem to achieve low equivalent oxide thickness. Inserting a well chosen metal layer between the poly-silicon and the dielectric is one of the solutions, which transform a pure silicon gate into a metal gate where the work function of the metal layer is a key factor The use of thin MOCVD tungsten nitride layers (10nm) to achieve the PMOS devices on 300mm wafers is pretty novel. Its integration into a complete gate stack (Poly-Si/TiN/WN/SiO@sub 2@ or highK) is quite challenging in terms of dry etch. In this work we focused on understanding the etch mechanisms of tungsten nitride in chlorine and fluorine based chemistries on a 300mm ICP tool, with in-situ optical emission spectroscopy and in-situ interferometer. We investigated the selectivity over several dielectrics (SiO@sub 2@ and Hafnium based material) on blanket wafers. Chemical analysis of the interaction layers were performed by X-ray Photoelectron Spectroscopy (XPS) on the involved materials. High selectivity numbers (@>=@50:1) were easier obtained on Hafnium based dielectric than on SiO@sub 2@, especially in fluorine based chemistries with the low volatility of the hafnium by products. Nevertheless, good enough selectivity numbers were also achieved on SiO@sub 2@ in fluorine chemistry at low bias voltage. The integration of the WN etch into a multiple steps process for sub 45nm metal gates was investigated in terms of CD & profile control by Scanning Electron Microscopy (SEM).

Plasma Science and Technology
Room 2009 - Session PS-MoA

Manufacturing and Scientific Challenges for Plasma Processing at 32 nm

Moderator: S. Shankar, Intel

2:00pm **PS-MoA1 Core Technologies for The Transition from Si Technology to Nano-technology*, H. Watanabe,*** Semiconductor Leading Edge Technologies, Inc. (Selete), Japan **INVITED**

Selete grapples with development of hp45/32nm module technology based on the results of Selete and MIRAI until now with promoting the variety project to meet widely the request which diversify. We take part in a new national project (MIRAI3) to develop the leading edge technologies of EUV lithography, post Cu interconnect, and robust transistor, and demonstrate the presence of Selete by worldwide preceding. In this presentation, I will introduce the challenge of Selete for 32nm module technologies and also discuss core technologies for the transisition from Si technology to Nano-technologies.

2:40pm **PS-MoA3 Patterning Technology for Sub-50 nm Memory Devices*, C.-J. Kang,*** SAMSUNG Electronics, Korea **INVITED**

In the era of sub-50 nm memory devices, patterning technology encounters many challenges, which arise from the introduction of immersion ArF lithography with high numerical aperture, a complex device structure, and the use of new materials. First of all, in the immersion technology, 100 nm thickness of ultra-thin resist process is used and it is likely to generate particles to cause defects. In addition, the reduction of a line width roughness (LWR) and overlay error between layers are getting more difficult. Second, in the plasma etching technology, the advanced features such as 3 dimensional FinFET structure force to develop a highly selective etching process. Finally, the introduction of new materials such as High-k dielectric, metal gate, and phase change materials are more challenging in the view point of profile and selectivity. Since the process window is getting narrow, control and monitoring technologies such as advanced process control (APC) and advanced equipment control (AEC) are strongly required. For the development and manufacturing of sub 50-nm memory devices, the patterning technologies should overcome many difficulties, which is related to not only the lithography and etching process itself, but also hardware development.

Plasma Science and Technology
Room 2009 - Session PS1+MS+NM-TuM

Plasma Patterning

Moderator: A. Agarwal, University of Illinois at Urbana-Champaign

8:00am **PS1+MS+NM-TuM1 Resolving Gate Patterning Issues at sub 65 nm Technology Nodes**, ***T.J. Kropewnicki***, *C.-C. Fu,* Freescale Semiconductor, Inc.

According to the 2005 edition of the International Technology Roadmap for Semiconductors, the physical gate length of high performance transistors at the 65 nm technology node is expected to be 25 nm in 2007, decreasing to 18 nm at the 45 nm node in 2010. Clearly, these goals present a clear challenge to photolithography and etch, which together are responsible for resolving these features on wafers. In addition to the pure scaling aspects of technology progression are the many additional enhancements such as stressors, which are being used to push the performance of silicon circuits. In certain integration schemes, these stressors add complexity to the transistor gate stack and accelerate photoresist bending and line collapse which cause etch masking, and ultimately variable, uncontrollable line widths. This paper will begin with a brief description of the transistor module process flow, highlighting the new challenges introduced to the gate stack etch at sub 65nm technology nodes. Next, a combination of enhancements in the gate photolithography and etch steps used to address these challenges will be presented. Results from these experiments will show a 50% reduction in across wafer line width variation, and a near 100% reduction in the incidence of polysilicon pattern distortion. Finally, the possible mechanisms for the increased levels of polysilicon pattern distortion seen with advanced transistor modules will be discussed.

8:20am **PS1+MS+NM-TuM2 Plasma Impact on ArF Resist Line Edge Roughness**, ***J. Thiault,*** LTM / CNRS France, France*; E. Pargon,* LTM / CNRS France*; J. Foucher,* CEA LETI France*; O. Joubert, G. Cunge,* LTM / CNRS France, France

As Critical Dimensions for semiconductor devices shrink too few tens of nanometers, the Line Edge Roughness (LER) or Line Width Roughness (LWR) becomes a critical issue because it can degrade resolution and linewidth accuracy that causes fluctuations of transistors performances. ArF resist patterns present a LWR of about 8 nm after lithography that is possibly transferred into the underlayers during plasma processing steps, resulting in a final LWR above the requirements of the International Technology Roadmap for Semiconductors (ITRS, which tolerates a LWR of around 3 nm for the 65nm technology node). In this study, isolated ArF resist patterns have been exposed to different plasma chemistries under identical processing conditions to investigate the impact of the plasma chemistry on the resist LWR. The sidewall roughness characterization has been performed using 3D Atomic Force Microscope (AFM3D) and top view Scanning Electron Microscope (CD-SEM). Experimental results tend to show that when the plasma/resist interaction is strongly chemically driven, such as in O@sub 2@ or SF@sub 6@ plasmas, with no bias applied to the wafer, the resist sidewalls are not smoothen. However, using plasma conditions where the ion bombardment component of the plasma is increased (by applying a bias power to the wafer), a LWR reduction is measured. This trend has been confirmed by exposing resist patterns to chemically inert plasmas such as Ar plasmas. Moreover, we have investigated plasma curing treatment on resist patterns, currently used in semiconductor manufacturing to reinforce the etching resistance of the resist. In this type of plasma (HBr based) where the ion current density is high and ion energy low, we also observe a decrease in LWR. All these trends suggest that the anisotropic ion flux is responsible for the smoothing of the resist sidewall roughness by eroding the bumps present on the resist sidewall.

8:40am **PS1+MS+NM-TuM3 ArF Resist Friendly Etching Technology**, ***T. Hayashi***, *Y. Morikawa, K. Suu,* ULVAC Inc., Japan **INVITED**

The requirements for dry etching technology in semiconductor processes beyond 90 nm node come to be very complicated and difficult. In photolithography, the introduction of ArF resist has started. ArF resists generally have very weak plasma resistance and are deformed in the etching process. However, as for the fundamental mechanism of deformation of resists in dry etching, sufficient discussions have not been done yet. So far ArF resist deformation has been thought to be caused by ion impinging damage. However, in our experiments, the deformation was not found in the high density NLD plasma in lower pressure than 1Pa, which gives relatively higher ion flux to the surface. So if ion energy is the main origin of the ArF resist deformation, then the NLD plasma might give a large resist deformation. Contrary to this expectation, however, the etched profiles in the NLD plasma showed low line edge roughness and almost nothing of striation. Considering these facts, the ArF resist deformation is clearly caused by concerted working of ion impinging damage and subsequent radical reactions at the resist-damaged area. This means if either of ion damage or radical reaction is nothing then the ArF resist deformation is nothing or is suppressed considerably lower. Therefore, the lower pressure process below 1 Pa or the lower reactive radical density process is necessitated. The latter is achieved by using highly effective radical scavenger. Generally H or CO has been used as the scavenger of F atoms. However, Br and I may be more effective as the scavenger, because Br and I react with F atoms and form stable inter-halogen compounds. So use of iodine or bromine contained perfluoro-hydrocarbon compounds like CF3I gives the ArF resist friendly etching process. Actually very smooth etched surfaces were obtained for patterned ArF resist/ARC/CAP/low-k/BARC/Si wafers. This work was partly supported by NEDO (New Energy and Industrial Technology Development Organization) in Japan.

9:20am **PS1+MS+NM-TuM5 Plasma Etching of Nano-Scale, Sub-10nm, Features**, ***Y. Zhang***, *C.T. Black, H.-C. Kim, E.M. Sikorski, T. Dalton,* IBM Research

Features Patterning nano-scale semiconductor features with precision imposes many new challenges for plasma etching. One of the challenges is that as the sizes of nano-scale features shrinking down to the sub-10nm regime, Plasma etching seems to approach to the limits. In this paper, we report the recent results of studying plasma etching of true nano-scale features using tow kinds of nano-sacle patterns. The first type of samples is diblock copolymer (similar to resist) self assembled nano holes and lines. The second kind samples are self-assembled organosilicate (similar to silicon oxide) nano patterns. With samples pattern, arrays of nano holes or nano lines' dimensions in the range of ~10nm, we studied plasma etching challenges for transferring nano-scale patterns into different materials (silicon, and silicon dioxide) in different plasma chemistries and process conditions. By varying the thickness of masks, the characteristics of aspect ratio dependence vs. "real" etching limits due to the sizes of sub-10nm nano-scale features were studied. The impacts of mask selectivity and line edge roughness (LER) to transferring sub-10nm patterns will be also discussed.

9:40am **PS1+MS+NM-TuM6 Nickel Atom and Ion Density in an Inductively Coupled Plasma with an Internal Coil**, ***L. Xu***[1], University of Houston*; N. Sadeghi,* University Joseph Fourier-Grenoble & CNRS, France*; M.K. Jain, S.C. Vemula, V.M. Donnelly, D.J. Economou, P. Ruchhoeft,* University of Houston

Nanopantography uses monoenergetic ion beams to enable massively parallel patterning of nano-sized features (e.g. 10 nm dia., 100 nm deep holes etched into Si). Deposition of metal nanodots (e.g. Ni) can have applications such as catalysts for the growth of an orderly array of carbon nanotubes. For this purpose, we have developed an inductive plasma source containing a relatively large fraction of Ni@super +@. A two-turn Ni coil immersed in the plasma generates a Ni-containing Ar plasma. Ni was sputtered both from the negatively self-biased coil and from a Ni target powered by a separate rf power. By adding a trace amount of N@sub 2@, gas temperatures T@sub g@ (= rotational temperatures) were derived from N@sub 2@(C-B) spectra. At low powers (capacitively coupled), T@sub g@ derived from the 0-0 band was erroneously high. This was attributed to energy transfer from Ar metastable atoms to the N@sub 2@ C (@upsilon@=0). At high powers (inductively coupled), both the N@sub 2@ 0-0 and 4-4 bands provided the same reasonable T@sub g@ because electron-impact dominates excitation at high power. Optical emission of Ar at 419.8 nm was used to estimate the plasma density, and was in agreement with values predicted from a global model. Ni densities were determined by optical absorption (using a Ni hollow cathode lamp) and were found to increase with pressure and power. The Ni@super +@ densities also increase at higher pressures and powers. Model predictions of Ni@super +@ densities are consistent with metastable Ni@super +@ densities derived from optical absorption. Finally, 50nm dia. Ni islands have been deposited in preliminary nanopantography experiments with the Ni@super +@ beam.

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

10:40am **PS1+MS+NM-TuM9 Bias Frequency Effect on SOC Film Degradation in sub-45 nm Line and Space Pattern SiO@sub 2@ RIE using S-MAP**, ***H. Hayashi***, *K. Kikutani, J. Abe, A. Kojima, T. Oohashi, I. Sakai, T. Ohiwa,* Toshiba Corporation, Japan

Sub-45 nm line and space pattern etching of SiO@sub 2@ film was studied using a stacked mask process (S-MAP) which consists of photoresist, spin-on-glass (SOG) and spun-on-carbon (SOC) film stacked structure. Maintaining pattern integrity becomes more challenging with the decrease of pattern size. Reduction of the hydrogen content of SOC, suppressed the fluorination reaction of its C-H bonds during SiO@sub 2@ etching which lead to line pattern wiggling, and as a result, 56 nm line and space pattern etching was realized.@footnote 1@ This time, the effect of ion energy distribution on SOC degradation in the SiO@sub 2@ etch process was investigated for sub-45 nm line and space pattern etching. The ion energy distribution was varied by dual frequency superimposed (DFS) RIE, using the conditions of 100 MHz rf supply with 3.2 MHz superimposed compared with 100 MHz with 13.56 MHz superimposed. The other SiO@sub 2@ etch conditions were the same, that is, C@sub 4@F@sub 8@ gas chemistry with the same electron density and self-bias voltage (-Vdc) of 6x10@super 10@ cm@super -3@ and 350 V, respectively. As a result, SOC line pattern wiggling was observed in the 3.2 MHz case, but it was suppressed in the 13.56 MHz case, even though the SiO@sub 2@ etch rates were 241 nm/min and 254 nm/min, respectively, and about the same. This shows that, by using DFS RIE with 13.56 MHz superimposed, SOC degradation can be suppressed while maintaining the SiO@sub 2@ etch rate for sub-45 nm line and space pattern etching. The maximum ion energy in the 13.56 MHz case should be lower than that of the 3.2 MHz case under the same -Vdc conditions, because with higher rf frequency, it would have a narrower ion energy distribution. In this way, SOC degradation was suppressed without decrease of the SiO@sub 2@ etch rate. In conclusion, S-MAP combined with 100 MHz/13.56 MHz DFS RIE realized sub-45 nm line and space pattern SiO@sub 2@ etching. @FootnoteText@ @footnote 1@ J. Abe et al., Symp. Dry Process, (2005) 11.

11:00am **PS1+MS+NM-TuM10 High Aspect Ratio (>10:1) Amorphous Carbon Layer Etching Using Soft Etch Capability in a High Frequency Capacitive Coupled Plasma Source Dielectric Etch Chamber**, ***S. Sung***, *J. Wang, S. Ma,* Applied Materials

Amorphous carbon layer (ACL) such as advanced patterning film (APF) is generally selected as one possible hard mask material for variety of dielectric etching application beyond 65 nm technology nodes to improve the etch process margin from reduction of resist thickness. Most of the APF etching application for DRAM, flash and logic technology are done typically on 1 µm film thickness to enable specific integration scheme of nanotechnology. The challenges of etching high aspect ratio ACL features are bowing prevention during etching, hard mask selectivity and the etch rate improvement for throughput concern. In this paper, high aspect ratio (HAR) contact through ACL layer is developed by soft etching capability using high frequency source plasma etch chamber. This development work was done in the dielectric etch chamber consisting of the superimposed dual bias power and a capacitive coupled source power > 100 MHz, which can be operated in either low density process regime for higher resist selectivity, or in high density process regime for profile control, resist integrity, minimal striations and effective chamber cleaning. With high frequency source power, fast etch rate >6000 Å/min of ACL has achieved with minimum hard mask corner chopping from small plasma self bias. All the process trends are characterized with profile control, hard mask selectivity and etch rate.

11:20am **PS1+MS+NM-TuM11 Chamber and Process Development of High Aspect Ratio Deep Trench Si Etch for DRAM Application below 60 nm**, *S. Barth, A. Henke,* Qimonda, Dresden, Germany*; A. Kersch,* Qimonda, Munich, Germany*; M. Reinicke,* University of Technology, Germany*; W. Sabisch,* Qimonda, Munich, Germany*; J. Sobe, A. Steinbach,* ***S. Wege***, Qimonda, Dresden, Germany

For Qimonda's DRAM Technology the deep trench etched into silicon is the base for the capacitor concept. The shrink of lateral dimensions at approximately constant capacity specifications leads to increased deep trench aspect ratio requirements. Therefore high selectivity to the etch mask and excellent uniformity is needed, especially for technologies below 60nm. In this paper we describe the development of a new DT plasma etch chamber and process to fulfill these requirements. Simulations (an equivalence circuit plasma model and surface reaction models) were combined with in-situ plasma measurement techniques (QMS, high resolution OES, IR absorption spectroscopy, SEERS and Langmuir probe sensor wafers) and technological experiments, to characterize hardware features and process conditions. To achieve high Si etch rate and selectivity, plasma density and electron energy distribution in the plasma bulk, and ion energy distribution on the wafer surface can be optimized through multi frequency cathode excitation. The selectivity is further enhanced by using advanced hard mask materials and combining of etching and deposition process regimes. Excellent uniformity has been achieved by new tool components, e.g., multi zone gas distribution and wafer temperature control. In addition, the etch process chamber includes new features for process control, in-situ wafer surface temperature and trench dept measurement. The equipment and process development was accomplished through close cooperation between Qimonda and the tool supplier.

Plasma Science and Technology
Room 2011 - Session PS2-TuM

Plasma Surface Interactions I: Joint AVS-AIChE Session

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

8:00am **PS2-TuM1 New Methods for Studying Plasma-Surface Interactions**, ***V.M. Donnelly***, *J. Guha, P.F. Kurunczi,* University of Houston **INVITED**

We have developed a new approach for studying plasma-surface interactions. A cylindrical substrate in the reactor wall is rotated at up to 200,000 rpm, allowing the surface to be repeatedly exposed to the plasma (about 40% of the time) and then analyzed in differentially pumped chambers in as little as 150µs after plasma exposure. Delayed desorption of products from the surface is detected by a chopped molecular beam mass spectrometer (MS), while adsorbates are observed by Auger electron spectroscopy (AES). Using these methods, we have studied oxygen and chlorine-containing plasma reactions on anodized Al. By varying the substrate rotation frequency, we can determine the overall kinetics of product formation and desorption. We observe desorption of Cl@sub 2@ in chlorine plasmas, O@sub 2@ in oxygen plasmas, and a mixture of Cl@sub 2@, O@sub 2@, ClO, and ClO@sub 2@ products in Cl@sub 2@/O@sub 2@ plasmas, due to recombination reactions on the surface. Absolute desorption yields are computed from calibrations based on the pressure rise in the differentially pumped MS chamber. We also detect chemisorbed Cl and O by AES in these plasmas, and find little dependence on substrate rotation frequency. From a combination of all these measurements it appears that recombination in pores of the anodized aluminum is responsible for the long decay time of desorbing products, and the relatively high probabilities for recombination. @FootnoteText@ P.F. Kurunczi Present affiliation: Varian Semiconductor Equipment, Gloucester, MA 01930.

8:40am **PS2-TuM3 Studies of Oxygen and Chlorine Atom Recombination Reactions on Anodized Aluminum in O@sub 2@/Ar, Cl@sub 2@ and Cl@sub 2@/O@sub 2@ Plasmas by a Spinning Wall Method**, ***J. Guha***, *V.M. Donnelly,* University of Houston

We have studied reactions of O and Cl atoms on a room temperature anodized aluminum substrate in O@sub 2@/Ar, Cl@sub 2@, and Cl@sub 2@/O@sub 2@ plasmas by the "spinning wall" technique. In this method, a rotating cylindrical substrate is periodically exposed to the plasma and then analyzed in a differentially pumped chamber by mass spectrometry (MS), and for the first time, by Auger electron spectroscopy (AES). By varying the %O@sub 2@ in Ar, O atom recombination has been studied over a wide range of O atom flux. In 600 W, 5 mTorr plasmas, the O@sub 2@ desorption signal decays in a "stretched" exponential manner over a 40 ms period by a factor of 8 for pure O@sub 2@ and by a factor of ~2 for 2% O@sub 2@/Ar. When a single desorption product is observed (e.g. O@sub 2@ in oxygen plasmas), we find that the pressure rise in the MS chamber as a function of increasing rotation frequency is directly proportional to the MS signal. Consequently, absolute fluxes of O@sub 2@ and Cl@sub 2@ could be obtained from a calibration of the pumping speed and ion gauge sensitivity. For the above example, the yields extrapolated to t=0 are 0.35 and 6 x 10@super 14@cm@super -2@s@super -1@, respectively. In pure chlorine plasmas, the Cl@sub 2@ desorption signal decays in a similar non-exponential manner, but by a larger factor of ~25 over 40 ms in a 5mTorr, 600W plasma, and with a higher yield of 3 x 10@super 15@cm@super -2@s@super -1@ extrapolated to t=0. Unlike O@sub 2@ or Ar, a substantial desorption of physisorbed Cl@sub 2@ is observed over 40 ms with the plasma off. Competitive recombination of Cl and O was also studied in Cl@sub 2@/O@sub 2@ plasmas. Formation of ClO and ClO@sub

2@ peak at ~80% O@sub 2@ and exceed O@sub 2@ and Cl@sub 2@ yields. In all experiments, chemisorbed O and Cl are detected by AES, and showed little dependence on substrate rotation frequency. A sub-surface diffusion-recombination model has been developed to explain these observations.

9:00am **PS2-TuM4 Plasma-Surface Reaction Mechanisms for Si Etching Profiles in UHF-ECR Cl@sub 2@/O@sub 2@, Cl@sub 2@/O@sub 2@/HBr Plasmas***, M. Mori,* *N. Itabashi,* Hitachi, Ltd., Japan*; K. Eriguchi, K. Ono,* Kyoto University, Japan

For fabricating beyond 45 nm-node ULSI devices, the nanometer-scale control of etching profiles is indispensable in Si etching processes, which in turn requires a better understanding of the mechanisms responsible for the feature profile evolution during etching. In this study, we analyze the mechanisms for Si etching by comparing the etched profiles with the profile simulation using an atomic-scale phenomenological model, which includes the effects of passivation layer formation, ion and neutral reflection on sidewalls, and chemical etching in addition to ion-enhanced etching.@footnote 1@ Experiments were performed by using an UHF-ECR plasma reactor in Cl@sub 2@/O@sub 2@/HBr mixtures, as a function of O@sub 2@ flow rate, Cl@sub 2@/HBr gas flow ratio, RF bias power, pressure, wafer temperature, and so on. The SEM and TEM results showed that the sidewall profiles became more tapered with increasing O@sub 2@ flow rate. The micro-trenching and footing (or sidewall bowing near the feature bottom) were found to be significant in Cl@sub 2@/O@sub 2@ plasmas, being suppressed with increasing O@sub 2@ flow rate; however, the sharp micro-trenching and footing disappeared in HBr/O@sub 2@ and Cl@sub 2@/O@sub 2@/HBr, and a weak lateral etch was observed on sidewalls in Cl@sub 2@/O@sub 2@/HBr plasmas. A comparison with the profile simulation indicated that the tapered profiles were enhanced by oxidization of re-incident etch products/by-products deposited on feature sidewalls. On the other hand, the micro-trenching was found to be attributed to the ion reflection on feature sidewalls; the footing was caused also by re-deposition of etch products on sidewalls from the feature surfaces being etched. Competition between etching reactions of chlorine and bromine and also between etching and passivation would be responsible for nanometer-scale control of the Si etching profiles. @FootnoteText@ @footnote 1@ Y. Osano, K. Ono, Jpn. J. Appl. Phys. 44, 8650 (2005).

9:20am **PS2-TuM5 Surface Reactions in Plasma Etching of Nitrided Hafnium Silicates***, R.M. Martin,* ***J. Liu,*** University of California, Los Angeles*; B. Xia, A. Misra,* Air Liquide*; J.P. Chang,* University of California, Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-65nm CMOS devices. Nitrided hafnium silicates (HfSiON) are promising since they combine the high dielectric constant and improved interface state density of hafnium silicates with the beneficial properties of silicon oxynitrides. In this work, chlorine-based chemistries are used in an electron cyclotron resonance high density plasma reactor to etch Hf-rich and Si-rich nitrided hafnium silicates, with 0 to 15 at.% of nitrogen. The plasma density, electron temperature, and gas phase species are characterized by a Langmuir probe, optical emission spectroscopy, and quadrupole mass spectrometry. The etching of SiO@sub 2@ and HfO@sub 2@ was first studied in Cl@sub 2@ and BCl@sub 3@ plasmas, to allow for studies of the etching of HfSiON with well controlled and varying compositions of Si and N in HfO@sub 2@. The etch rates of nitrided hafnium silicates were found to increase with the square root of ion energy, and the etching rate of films with 15 at.% of nitrogen is the highest. The surface chlorination was enhanced with increasing ion energy, ranging from 1 to 4 at.% of chlorine on the etched surfaces, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. The measured etching threshold energies were higher than that of pure HfO@sub 2@, suggesting that Si and N incorporation modifies film structure/density. In addition, while physical sputtering is the dominant mechanism in removing nitrogen as it was the lightest element of the four composing the film, more nitrogen remains on the surface of the Hf-rich films than the Si-rich films. This suggests that the removal of N is still related to its bonding within the film. The identity and distribution of the etch products will also be presented to elucidate the effect of Si and N on the removal of HfO@sub 2@.

9:40am **PS2-TuM6 Ion-Enhanced Plasma Etching of Hafnium Aluminates in Chlorine Based Plasmas***,* ***R.M. Martin,*** University of California, Los Angeles*; H.-O. Blom,* Uppsala University, Sweden*; J.P. Chang,* University of California, Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-65nm CMOS devices. Hafnium aluminates (HfAlO) have arisen as a promising material for gate oxide replacement due to their high dielectric constant, bandgap, and recrystallization temperature. Five compositions of hafnium aluminates were synthesized under this study with the Al@sub 2@O@sub 3@ content varying from 0 to 100%. An electron cyclotron resonance high density plasma reactor is used in this work to study the etching of hafnium aluminates in chlorine-based chemistries. The plasma density, electron temperature, and gas phase species are characterized by a Langmuir probe, optical emission spectroscopy, and quadrupole mass spectrometry. 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 co-sputter-deposited hafnium aluminate with well controlled and varying compositions of Al in HfO@sub 2@. 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. The etch rates of hafnium aluminates were found to increase with the square root of ion energy, and the surface chlorination was enhanced with increasing ion energy, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. In Cl@sub 2@ plasma, the dominant etch products were HfCl@sub 3@, HfCl@sub 4@, AlCl@sub 2@, and Al@sub 2@OCl, and the amount of chlorine on the etched surface increased with increasing ion energy, ranging from 0-2 at.%. In BCl@sub 3@ plasma, the etching rate was controlled largely by the dominant ion, BCl@sub 2@@super +@, with higher etch rates. The identity and distribution of the etch products in BCl@sub 3@ will also be presented to assess the effect of boron in patterning hafnium aluminates.

10:40am **PS2-TuM9 Ion-Radical Synergy in HfO@sub 2@ Etching Studied in a Beam Experiment***,* ***P.M. Gevers,*** *H.C.W. Beijerinck, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

The material HfO@SUB 2@ is one of the leading candidates to replace SiO@SUB 2@ as the dielectric material in gate stacks. Etching of HfO@SUB 2@ is currently under research, but mainly under actual plasma conditions. To get a more fundamental understanding of the etching properties, we studied Atomic Layer Deposited HfO@SUB 2@ under well-defined conditions in a multiple-beam experiment. The experiment consists of a thermal XeF@SUB 2@ beam and a low energy (50-1000 eV) Ar@super +@ beam. Real-time ellipsometry and mass spectrometry are used to measure etch rates, layer composition and etch products. The HfO@SUB 2@ etch rate is determined as a function of ion-to-radical flux ratios, ion energy and substrate temperature. Physical etching (sputtering) proves to be the main etching mechanism for HfO@SUB 2@ in the XeF@SUB 2@/Ar@super +@ chemistry. The F-radical does not etch HfO@SUB 2@ spontaneously, as can expected from the high boiling point of HfF@SUB 4@. The Ar@super +@ ion etch rate, however, can be increased by at least a factor of two in an F-chemistry, under specific temperature and ion-energy conditions. The ion-radical synergy varies from ion-dominated at room temperature/high ion energy to more chemically enhanced at elevated temperatures/low ion energy. Furthermore, during ion-etching, oxygen is preferentially sputtered which results in a non-stochiometric top layer. This is confirmed by an ex situ analysis of the atomic composition of the top layer. Based on these results we will present a simple model to describe the etching mechanism of HfO@SUB 2@ and discuss the promises of the F/Ar@super +@ chemistry for HfO@SUB 2@ etching.

11:00am **PS2-TuM10 Incorporation of the Kinetic Modeling into the 3-D Monte Carlo Profile Simulation***,* ***W. Guo,*** Massachusetts Institute of Technology, US*; H. Kawai, H.H. Sawin,* Massachusetts Institute of Technology

The translating mixed-layer kinetic model was translated into the 3-dimensional feature scale simulation. Kinetic parameters were determined by matching simulated etching yields with those experimentally obtained from etching experiments. Bearing in mind the characteristics of 3-D simulation, such as discretized cellular structure and discontinuous composition, we developed an algorithm to translate the kinetic modeling. For example, by separating different reaction mechanisms such as neutral-initiated or ion-initiated, it initiates different sets of reactions once a particle strikes the surface and products are removed according to reaction rates. By averaging the compositions among all neighboring cells around

the struck one, it resembles the layer translating down to the substrate. The simulator was able to predict the feature scale evolution as well as the etching yields by integrating the surface kinetics, the ion energy and angular dependence, and cell removal algorithm within the feature. A single stack of cells was used to test the performance of the simulator, with Si in Cl/Ar+, Si in Cl/Cl+, SiO2 in F/Ar+ chemistry at different neutral to ion flux ratios and energy levels. Etching yields and steady state composition were calculated and compared to the kinetic modeling results as well as experimental data. The results showed excellent agreement between experimental data, kinetic simulation and 3-D Monte Carlo simulation.

11:20am **PS2-TuM11 3-Dimensional Feature Scale Profile Simulation of Surface Roughness in Physical Sputtering Process*, H. Kawai,*** Massachusetts Institute of Technology*; W. Guo,* Massachusetts Institute of Technology, US*; H.H. Sawin,* Massachusetts Institute of Technology

One of the most important issues in the microfabrication process today is the line edge roughness (LER) on the sidewalls of gate electrodes in metal oxide semiconductor transistors. LER becomes more important as the feature size decreases because the variation in width becomes comparable to the minimum feature dimension. Sidewall roughening is also important in back-end processing, such as contact holes formation. A fundamental understanding of surface roughness and LER formation is necessary to optimize the IC manufacturing process. To promote this understanding, we have developed a 3-dimensional feature scale profile simulator to model and simulate the surface and sidewall roughening during the etching process of polysilicon and silicon dioxide in chlorine, hydrogen bromide and argon plasmas. A dynamic Monte Carlo model is used to simulate the etching process, where the simulation domain is discretized into an array of cubic cells with a unit cell length of 2.5 nm. The local surface conformation is determined by fitting the local region of the surface cells with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Our simulator has been utilized to examine the physical sputtering of a smooth polysilicon surface with argon ions at different off-normal ion incidence angles. Our results show that the root-mean square (RMS) roughness increases with the off-normal incident angle. In addition, at a normal ion incidence angle, the RMS roughness remained constant as the material was etched, but at grazing ion incidence angles, RMS roughness increased with the amount of materials etched. At high enough off-normal ion incidence angles, such as 75 degrees, the striations formed are aligned with the ion beam direction due to ion channeling. These results capture many of the qualitative trends observed in experimental measurements.

11:40am **PS2-TuM12 Modeling of Contact Hole Etching Profile in Two Geometrically Different Ways*, H. Fukumoto,*** *K. Ono, K. Eriguchi,* Kyoto University, Japan

To promote the etching technique for small-diameter contact holes, it is strongly required to understand the plasma-surface interactions more precisely. We have developed the contact hole etching profile simulation based on two different geometric structural models: one is a two-dimensional axisymmetric model, and the other is a two-dimensional planar one. These models took into account the transport of particles in microstructures and surface reactions therein through sputtering, ion-assisted etching, and deposition, where the feature profile evolution was represented by the cell removal method. In the simulation, CF@sub 4@ plasmas were assumed with different plasma conditions of ion temperature, density, and energy. The behavior of ions from the plasma onto substrate surfaces was characterized by the sheath thereon, the voltage of which was in the range 50-1000 V. The simulation domain was enclosed by the sheath edge and substrate surfaces of SiO@sub 2@ with an inert etching mask having hole patterns of 20-100 nm diameter. The surface chemistry was taken to depend on the energy, angle, and flux of incident ions and neutrals. The resulting etched profile of the bottom edge was more rounded in the axismmetric model than that in the planar one. In addition, the etch rate of deep or small-diameter features was slower in the axisymmetric model than in the planar one. These results are caused by the geometric difference between the two models; in practice, more fluxes of ions and neutrals are caught on feature sidewalls in the axisymmetric model than in the planar one. The axisymmetric model, which is more realized than the planar one, showed its advantage in the contact hole etching simulation.

12:00pm **PS2-TuM13 Enhancement of NF3 Etching Rates in PECVD Chamber Cleaning*, J.J. An,*** *B. Bai, H.H. Sawin,* MIT

In the optimization of PECVD chamber cleaning, it is important to maximize the cleaning rate and minimize the use of gases that are costly and must be treated. In conventional processes, much of the feed gases are not consumed in cleaning, but are lost by surface recombination and other processes. Using an Aston torroidal remote plasma source, we have shown the etching rate of silicon nitride using NF3 can be significantly enhanced by the addition of other gases in small amounts. The additives are composed of simple compounds providing selected amounts of C, S, and/or O to the mixture, with the performance depending on the choice and amounts of the additives. The nature of the enhancement will also be discussed. This enhancement is approximately a factor of four larger at lower silicon nitride temperatures. This lower temperature cleaning is particularly important since the chamber walls and pump exhaust tubing often require the longest time to clean. While the kinetics of this effect are not yet well understood, we will present mass spectrometer results sample by line-of-sight from the plasma source, FTIR measurements of the pump exhaust, as well as etching rate variation with gas compositions, flow rates, and sample temperature.

Plasma Science and Technology
Room 2009 - Session PS1-TuA

Emerging Plasma Applications

Moderator: J.B.O. Caughman, Oak Ridge National Laboratory

2:00pm **PS1-TuA1 Formation of Gas Barrier Films for Polymer Sheets with Metal Ion Source***, **Y. Nishido**, K. Nakamura,* Chubu University, Japan

The polymer film has been widely used for various practical applications as a light and cheap material. However there is a problem of air leakage caused by penetration of gas molecules due to low dense film property. On the other hand, a surface modification has been utilized as useful technologies to add functionalities to the materials. In particular, plasma-based ion implantation and deposition (PBII&D) allows us to improve adhesion of thin films serving the functionalities with an underlying substrate. In this study, fundamental investigations were carried out for applications of a metal ion source to formation of gas barrier dense films with the surface modification technique. An 13.56 MHz inductively-coupled argon plasma was produced for a typical pressure of several tens mTorr, and sputtered copper atoms were mixed into the plasma. The ionization fraction of the copper atoms increased with the argon pressure, and reached over ~90 % for the pressure higher than ~60 mTorr. Thus such a high pressure operation enabled the plasma to act as a copper ion source. Copper films were deposited on polyimide sheets as gas barrier films. To evaluate gas barrier characteristics, the deposited films were pressurized with Helium gas in two atmospheric pressures, and transmitted gas flow rates of Helium were measured with a differentially-pumped quadrupole mass analyzer (QMA). The deposition of the copper thin films made the gas leakage of the polyimide sheets significantly suppressed, and their gas barrier property was absolutely improved with an increase in thickness of the copper films. Furthermore, high-pressure operation (>30 mTorr) was preferable to suppression of the gas leakage, suggesting that the formation of the gas barrier films with metal ions is effective for improvement of the gas barrier properties.

2:20pm **PS1-TuA2 Room Temperature Crystallization of ITO Films on Glass and PET Substrates using RF Plasma***, M. Suzuki, Y. Shibayama, A. Kinbara, T. Watanabe, **H. Ohsaki**,* The University of Tokyo, Japan

Indium Tin Oxide (ITO) thin films were deposited by DC magnetron sputtering method at room temperature on soda-lime glass and polyethylene terephthalate (PET) substrates. X-ray diffraction (XRD) profiles indicate that the films have amorphous structure. The films were placed in a barrel-type discharge chamber having a pair of half cylindrical type electrodes installed in the proximity of the barrel wall and were exposed to a capacitively coupled RF(13.56MHz) discharge plasma for 10 minutes. The films were electrically floating during the plasma treatment. Although the temperature rise of the films during this treatment was less than 100°C, the films were crystallized and the XRD peaks were assigned to bixbite indium oxide peaks. The resistivity of the films decreased more than 50% after the plasma treatment. We found from the experimental results with changing the plasma treatment time that the crystallization starts at least 1 minute after the initiation of the plasma treatment and 2 minute treatment is enough to almost complete the crystallization. In order to investigate the effects of the gas component inclusions in the films on the crystallization, Quadrupole Mass Spectrometer measurements were carried out during the whole process. The effects of the carbon contamination, particularly generated from PET substrates will be discussed. Because amorphous ITO films have much smooth surface and our crystallization method does not change the surface roughness, we expect that our method is well applied to current-driven-type devices, like OLED and so on.

4:20pm **PS1-TuA8 Novel Technique for Processing Biomass by way of Atmospheric Pressure Plasma Processing***, **C.J. Oldham**, M.R. King, J.J. Cuomo,* North Carolina State University

Cellulosic materials are found in rich quantities in nature. The cellulosic materials represent a large natural resource of significant sugars for use in alcohols and other industrial products. Research on conversion of cellulosic materials such as corn stover, maple sawdust, cotton, switch grass, and others to alcohol has been heavily researched for the last few decades. Regardless of the amount of research devoted to these processes, there are problems associated with each and none are able to be scaled into an economically feasible process. Due to recent concern over energy prices and uncertainty in the oil supply, new interest has been generated for an economical process for producing alcohol from biomass. We have discovered that atmospheric pressure plasma can be used to disrupt the structure of biomass to efficiently release sugars from their binders by plasma enhanced "soft-hydrolysis". We have termed "soft-hydrolysis" to define a process for degrading cellulosic materials where in the conditions are less severe than current hydrolysis techniques. Due to radical formation in the plasma, degradation of the protective coating on the cellulosic material allows for access to the internal structure of value, i.e. the sugars in the material. Our results are significant due to the need for an alternative to current techniques requiring large concentrations of acid, high temperatures, and expensive enzymes. Plasma enhanced "soft-hydrolysis" represents a long felt need for an economical and ecological alternative for converting biomass to usable alcohols.

Plasma Science and Technology
Room 2011 - Session PS2-TuA

Etch for Advanced Interconnect II

Moderator: G.S. Oehrlein, University of Maryland

2:00pm **PS2-TuA1 Highly-Selective and Low-Damage, Damascene Processes in Robust Porous Low-k/ Cu Interconnects***, **H. Ohtake**,* Tohoku University, Japan **INVITED**

To reduce the cross-talk and power consumption among the on-chip interconnects, low-dielectric constant (low-k) films have been introduced. However, there are several problems on etching/ ashing process, such as the low etching selectivity to the mask, and the ashing damage of low-k film. In this paper, we will show 2 types of highly-selective and low-damage processes, (I) multi-hard-mask process and (II) advanced neutral beam process. We developed the 4 layered multi-hard-mask process without ashing damage. By controlling the radical ratio of carbon to oxygen, the etching selectivity to SiO@sub 2@ hard mask is kept high. The parasitic capacitance of Cu/ porous SiOCH in this process reduced about 7 % as compared with that in conventional via first DD process because of ashing-free process. The hard mask process is effective to reduce the damage, however, it is difficult to control the etching uniformity and hard-mask shouldering for various damascene structure. As an advanced process, we developed a newly advanced neutral beam system. The etching selectivity was drastically improved, and ashing damages were reduced significantly. We speculated that this is due to the elimination of exposure of ultraviolet light. Accordingly, the neutral beam system is a promising candidate for use in porous low-k damascene processes beyond 45nm node ULSIs.

2:40pm **PS2-TuA3 Plasma Confinement in Multi-frequency Plasma Process Chamber***, **K. Bera**, D.J. Hoffman, M. Kutney,* Applied Materials, Inc.

A production-worthy plasma process chamber needs to confine plasma to minimize chamber contamination, to reduce cleaning time and cost, and to minimize process drift. The process chamber needs to achieve high flow rate at low pressure for critical etch applications. One method to confine plasma can be the use of slotted confinement ring. However, a slotted confinement ring generates significant pressure gradient that prohibits low pressure high flow operation. In addition, ignition of plasma in the peripheral region can lead to process drift that is detrimental to process performance. An annular confinement ring design confines plasma for both VHF and HF operating conditions. The annular ring design is optimized using plasma and flow simulations to ensure plasma confinement and enhance flow conductance. Higher flow conductance leads to lower pressure on the wafer enhancing operating window that allows us to achieve desired process characteristics for critical etch processes. The annular confinement ring avoids parasitic plasma improving productivity. To further enhance plasma confinement, an innovative concept of impedance confinement has been analyzed using plasma simulation. An impedance parameter has been defined, and optimized so as to achieve highly confined plasma. The optimized design of confinement ring with impedance confinement is implemented and verified experimentally for both VHF and HF operating conditions. Annular confinement ring design with impedance confinement not only confines plasma to minimize chamber contamination, reduce cleaning time and cost, but also avoids parasitic plasma to improve productivity, and increases flow conductance to enhance operational window.

3:00pm **PS2-TuA4 Scaling of Dual Frequency Capacitively Coupled Plasma Etching Tools Above 100 MHz****, **Y. Yang**, M.J. Kushner,* Iowa State University

Capacitively coupled dual frequency reactive ion etching reactors allow, in principle, independent control of the ion flux and ion bombardment energy

which is important for obtaining high selectivity. There is great interest in extending the high frequency to values approaching or exceeding 100 MHz to increase the proportion of power dissipated in electron heating while lowering the electron temperature. These trends are believed to produce more favorable dissociation pathways in, for example, fluorocarbon etching. In this talk, results will be discussed from a computational investigation of dual frequency RIE reactors for high frequencies exceeding 100 MHz. This study was performed with a two-dimensional hybrid-fluid model. To properly address the coupling between the electric field and electron transport under high frequency conditions, a fully implicit electron transport algorithm was developed. Spatially dependent electron energy distributions generated by a Monte Carlo simulation, which properly captures the high frequency heating, provide excitation rates. Results from studies in rare gases and fluorocarbon gas mixtures (e.g., Ar/C@sub 4@F@sub 8@/O@sub 2@) will be presented as a function of the high frequency while keeping power constant. Assessments of the change in dissociation pathways, radical fluxes; and ion energy and angular distributions to the substrate will be presented. @FootnoteText@ *Work supported by the Semiconductor Research Corp. and the National Science Foundation.

3:20pm **PS2-TuA5 Patterning of Narrow SiOCH Trenches using the Late Porogen Removal Process***, **T. Chevolleau,*** LTM-CNRS-France, France*; D. Eon,* CNRS-LTM-France*; M. Darnon,* CNRS-LTM-France, France*; T. David,* CEA-LETI-France, France*; L. Vallier,* CNRS-LTM-France*; O. Joubert,* CNRS-LTM-France, France

In CMOS technology, the dominant strategy to achieve future generation of ultra low-k interlayer dielectric materials with a dielectric constant close to 2.2 is to introduce porosity into a SiOCH matrix. However, porous materials are very sensitive to ash and etch plasma exposures and one of the integration challenges is to reduce the impact of these plasma processes on the low-k modification. To solve this issue, one of the emerging solutions is the late porogen removal process. In this approach, the porosity in SiOCH is generated by a sacrificial porogen (carbon based polymer) which is desorbed after patterning or copper filling. These hybrid materials are expected to behave like non-porous SiOCH materials during the etching processes. In this work, the etch mechanisms of the hybrid material and the patterning of narrow trenches down to 50 nm using a metallic hard mask are studied. The etching is performed in an industrial capacitively discharge reactor using a fluorocarbon-based plasma. A parametric study on blanket wafers shows that the etch mechanisms are similar to those of a dense SiOCH material. However, surface analyses by XPS reveal that the higher carbon content in the hybrid material induced by the presence of porogen leads to the formation of a thicker fluorocarbon overlayer than with typical dense SiOCH materials. Consequently, the etching is very sensitive to the addition of polymerizing gas which can potentially lead to etch stop phenomena. The patterning of narrow trenches in hybrid materials shows that etch profiles are similar than in dense SiOCH layers. The main issue is the profile distortion induced by etch products redeposition on the trench sidewalls. XPS analyses are also conducted on the bottom and sidewalls of the trenches using the chemical topography analysis technique. The selectivity to the underneath etch stop layer (SiC) remains low (of about 4) indicating that the use and the development of a specific over etch step is required.

3:40pm **PS2-TuA6 Profile Control and Sidewall Modifications of Narrow Porous ULK Trenches after Plasma Etching and Pore Sealing Treatments***, **M. Darnon**, T. Chevolleau,* CNRS-LTM-France, France*; D. Eon,* CNRS-LTM-France*; F. Bailly,* CNRS-IMN-France, France*; L. Vallier,* CNRS-LTM-France*; J. Torres,* STM-France*; O. Joubert,* CNRS-LTM-France, France

In CMOS technology, for most of the interlayer dielectric materials, low k values are obtained by introducing porosity in order to reduce the total resistance capacitance delay in the interconnect levels. Trench or via patterns are currently transferred into porous SiOCH (p-SiOCH) using a dual hard mask strategy. In this work, we have investigated the profile control in narrow trenches etched using a metallic hard mask, and the characterization of the dielectric material degradation induced by the etching and pore sealing processes. The stack investigated is composed of 600 nm p-SiOCH, 40 nm SiO@sub 2@, 45 nm TiN and 100 nm photoresist (PR). The 200 mm wafers are patterned using direct ebeam lithography to achieve aggressive trenches dimensions down to 50 nm. The etching of p-SiOCH trenches is performed in a Magnetically Enhanced Reactive Ion Etcher (MERIE) using fluorocarbon gas mixtures. Pore sealing treatments on the patterned structures are achieved in a CH@sub 4@ or NH@sub 3@ plasma. Trenches profiles are observed by Scanning Electron Microscopy (SEM). Sidewalls and bottom surface composition are determined using chemical topography analysis by X-ray Photoelectron Spectroscopy (XPS). A parametric study reveals that profile distortions are attributed to by-products redeposition and hard mask faceting. The by-products redeposition is minimized by increasing the wafer temperature and/or using low polymerizing chemistries. The faceting is strongly reduced by lowering the ion bombardment. Whatever the etching conditions, the porous materials are modified on the trenches sidewalls. After narrow trenches etching with the optimized etch conditions, the impact of the pore sealing plasma treatments on the sidewalls and bottom modification is investigated. XPS analyses reveal that the pore sealing is attributed to the formation of a carbon rich layer with CH@sub 4@ plasma or a SiO@sub x@ layer with NH@sub 3@ plasma.

4:00pm **PS2-TuA7 Three-Dimensional Control of Interconnect Features: Sidewall Roughness Transfer During Patterning Processes***, **T. David,*** CEA-LETI-France, France*; J. Foucher, N. Posseme, A. Jacquier, A.-L. Fabre,* CEA-LETI-France

Dimensional control is a key challenge for present and future interconnect technology generations. The dominant architecture, damascene, requires tight control of patterning. To extract maximum performance, interconnect structures cannot tolerate variability in profiles without producing undesirable RC degradation. For advanced nodes, feature size effects, such as electron surface scattering, will increase the effective resistivity and may require new technological development. Indeed characterization shows significant contributions to resistivity by scattering from both grain boundaries and sidewall patterns. In this work, we investigate the sidewall roughness (LWR, LER) transfer during interconnect patterning. The roughness is first calculated by performing threshold analysis of top down SEM images. However this technique does not take into account variations along feature height. Therefore, we have used a new 3D CD-AFM (Dimension X-3D) which enables us to characterize roughness along the features after each technological step of C065 etching processes on 300mm wafers. Trenches with various dimensions are patterned with conventional ArF photoresist. Then, the patterns are transferred into a metallic hard mask before etching of capping and dielectric layers. First results show a decrease of LWR during lithography pattern transfer into the metallic hard mask. Moreover LWR stays constant along profile height during capping and dielectric etching. Regarding LER, it seems that a slight increase is observed when going from the dense dielectric material (capping layer) to the more porous one (dielectric layer) while keeping LWR constant.

4:20pm **PS2-TuA8 Dry Etch Process of Contact holes using Multi-Functional Hard Mask***, **W.K. Kim,*** Hynix, Korea*; S.K. Lee,* Hynix, Korea, Republic of Korea*; J.H. Cho, J.H. Sun, K.L. Lee, G.S. Lee, S.C. Moon, J.W. Kim,* Hynix, Korea

As feature size continuously shrinks, pattern collapse has dramatically increased, which has led to decrease photoresist thickness and use hard mask materials as a pattern transfer layer. Amorphous carbon (a-C) is expected to be used in the nano technology regime because of its strong merits such as superior etching durability and low damage during strip. However it is not cost effective and complex in dry etching process. To overcome these problems, many of researchers focus on the new material development. Multi-functional hard mask (MFHM) is very useful in terms of cost reduction and process simplicity compared to a-carbon process. We call Si-ARC as a MFHM because it has to have both functions of anti-reflective and pattern transfer layer. We have evaluated the reactive ion etching characteristic of MFHM on spin-on carbon (SOC). In this study, we planned to form very fine pattern semiconductor of sub-80nm technology and beyond in combination of N2/O2 or N2/H2 without additional etching gas. The stack tested in this study was a Photoresist (100-150nm) / MFHM (100-200nm) / SOC (500-800nm) on insulator film (~2500nm). We focused on investigating etch rate, etch selectivity and etch profile. These are highly dependant to the polymer types of MFHM, SOC grain size, and Si content in MFHM. We also found that MFHM having Si-O-Si bond showed higher etch selectivity than that having Si-Si-O bond if their Si content is same. The small grain size in SOC and high Si content in MFHM are required to get better selectivity and profile. Especially, we obtained vertical fine pattern contact holes with minimized bowed profile by using N2/O2 plasma only and by partially oxidizing MFHM to SiO2-like surface (SiON layer in case of a-C process). We confirmed the surface of MFHM was oxidized about 10~50nm in depth during etching process using AES, XPS, and TEM observation

Plasma Science and Technology
Room 3rd Floor Lobby - Session PS1-TuP

Etching of High-K, Compound Semiconductors and Advanced Materials Poster Session

PS1-TuP1 Influence of Redeposition on the Plasma Etching Dynamics*, L. Stafford,* University of Florida*; **J. Margot,*** Université de Montréal, Canada*; S. Delprat, M. Chaker,* INRS-Energie, Matériaux et Télécommunications, Canada*; S.J. Pearton,* University of Florida

The development of high-resolution pattern transfer processes is one of the critical issues related to the manufacturing of very large scale integrated circuits. As the feature size moves toward the nanometer scale, the commonly used trial/error method for the optimization of dry etching is clearly approaching its limit, and basic understanding of the plasma etching science has become crucial for process control. Basic understanding can be realized for example by developing rate and feature scale models which by comparison of their predictions to experimental data can provide insights into the plasma etching dynamics, and eventually suggest experimental conditions for reliable pattern transfer. In this presentation, we examine the influence of redeposition on the plasma etching dynamics using both experimental and modeling approaches. Redeposition of sputtered species is a common feature in plasma etching and usually leads to the formation of shallow sidewall angles and fences on the sidewall of etched profiles. Even though redeposition is known to play an important role in several plasma etching processes, no quantitative results on the influence of this phenomenon have been reported so far. This work reports on measurements of the redeposition degree during sputter-etching of Platinum (Pt), Barium-Strontium-Titanate (BST), Strontium-Bismuth-Tantalate (SBT), and Photo-Resist (PR) in a high-density argon plasma. While PR exhibits a redeposition-free behaviour, the redeposition degree of Pt, BST, and SBT increases from 10 to 90% as the argon pressure increases from 0.5 to 10 mTorr. The physical mechanisms yielding the observed redeposition effects are discussed. Based on these results and using other experimental data reported in the literature, it is demonstrated that, depending on the plasma etching conditions, redeposition effects can induce misinterpretation of the etch rate data. A rate model taking into account redeposition effects is proposed.

PS1-TuP2 Damage Recovery of (Bi@sub4-x@La@subx@)Ti@sub3@O@sub12@ Thin Films during the Etch Process using Inductively Coupled Plasma Sources*, **J.G. Kim**, G.H. Kim, K.T. Kim, C.I. Kim,* Chung-Ang University, Korea

Ferroelectric thin films are employed for ferroelectric random access memories (FeRAMs). FeRAMs offer non-volatility, a lower voltage operation and larger write cycle numbers. (Bi@sub4-x@La@subx@)Ti@sub3@O@sub12@ (BLT) thin films were proposed as a promising ferroelectric material that does not exhibit the polarization fatigue, does have bigger remanent polarization value than that of SrBi@sub2@Ta@sub2@O@sub9@. Moreover, it does not contain the lead contents which occurs environmental disruption. Accordingly, for high density FeRAMs, the etching mechanism of BLT thin films and surface damage during the etching process must be understood. Moreover, damaged films during the etch process should be improved. However, although the etching mechanism was already examined in several researchers, etch damages of BLT thin films and its recovery was not established. In this work, the etch damages of BLT thin films in inductively coupled plasma were investigated with various gas mixing ratios, ICP powers, and bias powers. The etch rates were measured using a surface profiler. For investigating the effects of O@sub2@ plasma, O@sub2@ addition was performed during the etching and etched samples which did not add O@sub2@ gas were treated in the O@sub2@ plasma. After the etching process, the leakage current was measured by parameter analyzer. To evaluate plasma induced physical damages, the changes of lattice of etched BLT samples were evaluated with x-ray diffraction. The precision workstation ferroelectric test apparatus was used for measurement of P-E hysteresis curves. Also the etched surface roughness was evaluated by atomic force microscopy and scanning electron microscope.

PS1-TuP5 Etch Characteristics of Na@sub 0.5@K@sub 0.5@NbO@sub 3@ Thin Films using Cl@sub 2@/BCl@sub 3@/Ar Inductively Coupled Plasma*, **C.M. Kang**, K.T. Kim, G.H. Kim, C.I. Kim,* Chung-Ang University, Korea

Recently a unique combination of properties has been discovered in the perovskite Na@sub 0.5@K@sub 0.5@NbO@sub 3@(NKN) thin films. They possess very low loss at room temperature, high piezoelectric coefficient, and moderate dielectric constant, which is strongly dependent on electric field. It was shown that NKN thin films are able to overcome the drawbacks of other materials, such as (Sr,Ba)TiO@sub 3@ and Pb(Zr,Ti)O@sub 3@ for nonvolatile memory applications. Additionally, NKN films exhibit a self-assembly phenomenon despite high volatility of Na and K constituents, strongly c-axis oriented ferroelectric films can grow onto the Si substrates. NKN films are promising for a vast variety of emerging applications, such as nonvolatile memory and actuators. But, etch properties and etching mechanism of NKN have not established yet. In this study, we studied etch characteristics of NKN thin films using inductively coupled plasma for ferroelectric random access memories. The etch rate and etch selectivity in proportion to variations gas mixing ratios, input rf power, dc bias voltage and chamber pressure were obtained. As the ICP power and the rf power increased, the etch rate of NKN also increased. As the gas pressure increased, the etch rate of NKN decreased. The behaviors of active species in plasma were measured by optical emission spectroscopy (OES). Scanning electron microscopy (SEM) was used to investigate the etching profile. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical states of the etched surfaces.

PS1-TuP7 The Etching Characteristics of High-K Dielectric Materials using the Neutral Beam Etching System*, **K.S. Min**, B.J Park, C.K. Oh, S.D. Park, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea

High-k dielectric materials are attractive as a gate dielectric for MOSFETs device because they have wide band gap, superior thermal stability, and low-leakage-current. However, the integration of the high-k dielectric materials is one of the important issues in scaling MOSFET device for the critical dimensions below 50nm. In this study, the etching characteristics of high-k dielectric materials (HfO@sub 2@, Ta@sub 2@O@sub 5@) were studied using a reactive neutral beam. The energetic reactive neutral beam used in this study was formed by reflecting the reactive ions on a planar reflector at a low angle extracted by a reactive ion gun. The etch rate and selectivity between Si and high-k dielectric materials were investigated as a function of reactive gas mixture ratio. Also, the changes in the surface stoichiometry of high-k dielectric materials were measured using an angle resolved X-ray photoelectron spectroscopy (ARXPS) and compared with the surface stoichiometry of the high-k materials etched by inductively coupled plasma etching. ARXPS data showed that the changes in the surface composition of high-k dielectric materials by the neutral beam etching were significantly less compared to those by conventional inductively coupled plasma etching.

PS1-TuP8 Selective Etching of Titanium Nitride*, **D.J. Wu**, E.J. Karwacki,* Air Products and Chemicals, Inc.

Titanium nitride (TiN) has many emerging new applications within semiconductor industry. For example, it is already being employed as a metal electrode in DRAM devices, and as a barrier material within logic devices. TiN film can be made using either chemical vapor deposition or atomic layer deposition based processes, where a quartz tube furnace is often used as the deposition reactor. After film deposition, a cleaning process is typically utilized to remove TiN residues. The cleaning process needs to be fast enough to meet the requirements in high volume manufacturing and selective enough to prevent damage to the underlying quartz. Damage such as etching of the quartz will cause surface roughening that may then interfere with heat transfer through the quartz walls to wafers within the reactor. Using a lab reactor with both thermal and remote plasma capabilities, a variety of reactive gases and process conditions were screened for selectively etching TiN. In this paper we report on our development of two thermally assisted processes: a plasmaless process using XeF2 and a remote-plasma process utilizing NF3 in combination with xenon. The XeF2 process provides high etch selectivity for TiN vs quartz at a moderate TiN etch rate. The remote plasma process using NF3 and Xe increases the etch selectivity by an order of magnitude and doubles the etch rate when compared to a NF3 only remote plasma process.

PS1-TuP9 Improvement of External Efficiency using Surface Roughening Technique in the GaN-Based Light Emitting Diodes*, **H.C. Lee**, J.B. Park, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea

Gallium nitride based materials have attracted considerable interest in relation to their potential use in optoelectronic devices, such as light emitting diodes(LEDs) and laser diodes. Recently, as the brightness of GaN-based LEDs has increased, applications such as displays, traffic signals, backlights for cell phones, exterior automotive lighting, and printers have become possible. In general, the internal quantum efficiency for GaN-based

LEDs is far smaller than 100% at room temperature due to the activation of nonradiative defects and it is also well known that the external quantum efficiency is still much smaller than the internal quantum efficiency. The external quantum efficiency of GaN-based LEDs is low because the refractive index of the nitride epitaxial layer differ greatly from that of the air. The refractive indexes of GaN and air are 2.5 and 1.0, respectively. The critical angle for the light generated in active region to escape is about 23degree. Surface roughening of a LEDs is one of the methods for improving the light extraction. Fujii reported an increase in the extraction efficiency of GaN-based light emitting diodes by surface roughening. In this study, we investigated on the improved light output and electrical performance of a GaN-based LEDs by a roughened surface using etching technique. The light output efficiency of a LEDs structure with a roughened surface was significantly increased compared to that of a before roughened LEDs structure. The structural and electrical properties of the surface roughened of the LEDs were evaluated using a scanning electron microscope and a HP4145A probing system. Optical properties such as intensity and wavelength of the emitting-light was observed by an optical emission spectroscopy(OES). Output power of samples was measured by an optical powermeter.

Plasma Science and Technology
Room 3rd Floor Lobby - Session PS2-TuP
Etching and Process Integration Poster Session

PS2-TuP1 Development of a Dry Etching Profile Simulator in a High-Density, Low-Pressure Plasma*, **J. Saussac**, A. Quintal-Leonard, J. Margot,* Université de Montréal, Canada*; M. Chaker,* INRS-Energie, Matériaux et Télécommunications, Canada

The development of new sub-micron technologies requires a fundamental understanding of device fabrication processes in order to be able to push the technology to its limits. In this context, numerical simulations are of great interest for providing insights into the physics underlying various processes and therefore helpful for optimizing the experimental conditions. Our ultimate purpose is to develop a 2-dimensional plasma etching simulator devoted to the determination of the etch profile evolution of complex oxides in a high-density reactive plasma. Our approach consists in a two dimensional cellular discretization of the plasma, mask and material domains; each cell is initially set to the same size and includes the same number of atoms. Ion transport from the plasma to the surface is simulated by a Monte Carlo technique. Testing of the model is performed by comparing its predictions to existing experimental measurements of silicon sputter-etched patterns. As only pure physical etching is considered, the atomic population of each cell evolves according to the etch yield, the cell passing from an unetched to an etched state when the number of atoms by cell falls below a threshold. Once the model validated for silicon sputter-etching, it is planned in a second step to introduce in the model the chemical aspects required to investigate the etching of complex oxides like SrTiO@sub 3@ in a halogenated plasma.

PS2-TuP3 A Comparative Study of Wafer Edge, Backside and Bevel Etching Properties for Oxide, TiN and Amorphous Carbon Films with Torus-Shaped Capacitive Coupled Plasma Source*, S.-H. Cho, **J.-H. Yang**, I.-S. Choi, J.-K. Kim, H.-J. Lee, B.-H. Choi, J.W. Kim,* HYNIX Semiconductor Inc, Republic of Korea

The film residues polymer that are generated during the semiconductor device processing on the wafer edge, backside and bevel area are known to be severe particle source. These areas need to be cleaned to prevent the particle from inflowing into the pattern area. In this study, the bevel etching properties for oxide, TiN and amorphous carbon film with torus-shaped capacitive coupled plasma source are examined to find ways to remove harmful film residues polymer on the wafer edge, backside and bevel area. The optimum plasma process conditions without plasma damage on wafer pattern area will be discussed as a function of processing parameter such as pressure, power and gas ratio.

PS2-TuP5 Etching of Ultra-low-k BEOL Material with High Density Plasma*, **T. Nishizuka**, T. Nozawa,* Tokyo Electron, LTD., Japan

As the design rule of device is evolved, k value of BEOL dielectric material is required to be lower, and its mechanical strength and plasma resistance become also lower. For the current generation whose k is 2.7~3.0, plasma condition of dielectric etching can be still similar to SiO2 etching condition with low plasma density and high ion energy. For the future generation whose k is less than 2.5, however, different plasma condition with high density and low energy is supposed to be applicable since the material become like organic and porous. In this study, we examined RLSA (Radial Line Slot Antenna) microwave plasma to low-k etching, and found extremely low ion energy (RF bias Vpp<250v) resulted in smooth resist mask surface and via sidewall keeping enough etch rate. Furthermore it appeared that the selection of bias power frequency was effective to RIE lag control.

PS2-TuP6 Study on the Plasma Damage by Spacer Oxide Etching of MOSFET Device*, **H. Ahn**, J.S. Lee, S.B. Kim, K.D. Kim, B.H. Lim, D.G. Choi, D.S. Kim, Y.W. Song, J.W. Kim,* HYNIX Semiconductor Inc., Republic of Korea

Plasma etching is widely-used tool for the manufacturing of large scale integrated electronic device. In dry etching process, the plasma damage is able to cause dielectric breakdown or severe change of electrical properties, such as threshold voltage, breakdown voltage, and so on. Recently, the researches on these areas have been widely studied, it is well known that uniform plasma is the best solution to minimize charging effect. In this paper, the impact of plasma damage on the MOSFET during spacer oxide etching that is necessary for the formation of LDD structure MOS transistor after deposition of sidewall dielectric layer is studied. Especially, this work focused on the damage effect of on-off transient from the viewpoint of device parameter. Physical properties are characterized by Secondary Ion Mass Spectroscopy (SIMS), Transmission Electron Microscopy (TEM), Auger Electron Spectroscopy (AES) and so on. It is found that on-off transient damage is one of the most important factor to affect the PMOS device characteristics.

PS2-TuP7 Plasma Chemistries for High-Aspect-Ratio Dielectric Etching Beyond 65 nm Node*, **T.L. Anglinmatumona**,* San Jose State University*; C.T. Gabriel,* Advanced Micro Devices

The transition from saturated (c-C4F8, C-C) to unsaturated (1,3-C4F6, C=C) plasma gases was found to lessen the challenges of low selectivity and ARDE. The shrinking diameter of the via-hole due to scaling feature sizes is inducing an austere list of etch challenges. Saturated chemistries are known to generate large molecular-weight radicals that lead to poor etch performance with increasing aspect ratios. Due to the changing dynamics of device sizing, saturated chemistries offer limited etch performance which is mainly driven by their high energy thresholds and bond decomposition scheme. Data in this research show the chemistry of hexafluorobutadiene (1,3-C4F6) is helping to enable good etch performance with increasing aspect ratios beyond 65 nm. The etch selectivity was improved by 2X. ARDE was reduced and showed a via-depth improvement of 11.5%.

PS2-TuP8 Formation of Silicon Nitride Nano-Pillar Hard-Mask Patterns in Dual-Frequency Superimposed Capacitively Coupled Plasma and Their Application to Nano-Scale Si Etching*, **C.K. Park**, C.H. Lee, H.T. Kim,* Sungkyunkwan University, Korea*; N.-E. Lee,* Sungkyunkwan University, korea

Fabrication of silicon nano-scale structures has attracted much interest because of distinctive differences in the etch properties of these nano-scale hole compared with large-size diameter hole (@>=@ 100 nm). However, it is difficult for conventional optical lithography techniques to make patterns smaller than a light wavelength. Nano-scale etching using nano-pillars formed by non-lithographic method can be very useful for under standing the etch characteristic of nano-scale patterns. In this work, we investigated nano-scale etching of silicon pattern with the diameter less than 30-nm using the silicon nitride nano-pillars as hard-mask or lift-off mask. Silicon nitride layers were etched with CH@sub 2@F@sub 2@/H@sub 2@/Ar dual frequency superimposed capacitively coupled plasma (DFS-CCP). During the etching process the CF@sub x@ polymer nano-dots are formed on silicon nitride surface, which leads to the formation of silicon nitride nano-pillars. Nano-scale Si pillar etching using the silicon nitride nano-pillar hard-mask or Si hole pattern etching using polymer mask generated by lift-off method were carried out. Etching characteristics of nano-scale silicon patterns will be discussed in detail in conjunction with the silicon nitride nano-pillar hard-mask fabrication.

PS2-TuP9 Development of Dual-Frequency Inductively Coupled Plasma and Control of Plasma Parameters Changing the Power Ratio between High- and Low-Frequency rf Sources*, **S.-H. Seo**,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H.-S. Lee,* Korea Advanced Institute of Science and Technology, South Korea*; H.-Y. Chang,* Korea Advanced Institute of Science and Technology

A novel dual-frequency inductively coupled plasma source which was developed for high-density plasma CVD process was presented. Two coaxial

planar-type antennae consisting an outer single-turn antenna with a diameter of 300 mm and an inner multi-turn antenna were used for the plasma generation and applied by two rf powers with different frequency. The two rf power sources with the frequencies of 2 and 13.56 MHz respectively were used in the experiment. A Langmuir probe with four chock filters for the rf compensation for the primary and the second harmonic rf noises of each frequency was used to characterize the dual-frequency inductive plasma. It was found that the electron temperature can be controlled by changing the power ratio between two rf sources and is ranged within the electron temperatures achieved in the single-frequency inductively coupled plasma with each frequency. Also, the power ratio between two frequencies and the configuration of two antennae was found to control the plasma uniformity in the radial direction. Here, the experimental results such as the diagnostic and CVD process results will be presented and the effect of two rf powers on the plasma characteristics and the CVD process will be discussed.

PS2-TuP10 Silicon Surface Treatment of Contact Hole in Memory Device by Downstream Plasma*, **C.W. Kim,*** PSK-inc, Korea, Korea, Republic of*; C.W. Lee, H.B. Seo, K.T. Kim, J.K. Yang,* PSK-inc, Korea

Silicon surface of contact hole has been treated by fluorine based plasma using downstream type ICP source. Silicon etch rate and uniformity had been investigated on 12 inch blanket wafer as a function of process parameters. The profile of etch rate map is changed from center high to edge high etch rate tendency by controlling total gas flow rate and this make it possible to control etch uniformity. The etch selectivity of silicon to silicon nitride, as SAC barrier material, is studied with the various gas mixture ratio of feed stock gas. Commonly higher etch selectivity is obtained under the high silicon etch rate condition due to the difference of etch characteristics between silicon and silicon nitride film but higher selectivity more than 7:1, silicon to nitride, can be achieved over wide range of silicon etch rate by adjusting gas mixture ratio. Finally, the etch uniformity and etch profile of bit line contact and storage node contact hole is examined by TEM on 12 inch whole pattern wafer.

PS2-TuP11 The Behavior of Polymer Film Deposition during Etching the Oval Contact Holes*, **S.-I. Cho,*** Samsung Electronics Co. LTD, South Korea*; S. Lim,* Samsung Electronics Co. LTD, Korea*; H. Baik,* Samsung Advanced Institute of Technology, Korea*; Y. Lee, C.-J. Kang, H. Cho, J.-T. Moon,* Samsung Electronics Co. LTD, Korea

Recently, the distorted pattern transfer during the high aspect ratio contact etching process has been reported. The reason of the deformation seems to be the result of non-uniform polymer deposition and/or the deflection of ion trajectory. This study is intended to clarify the behavior of the polymer deposition and its effect on the pattern deformation. The thickness of the polymer films on the sidewall of oval holes after etching was measured by cross-sectional TEM and SEM. The samples with carbonic masking layer were prepared after etching with C4F6, Ar, and O2 chemistry. The aspect ratio of the holes was 15. The thickness of the deposited film is variable with respect to the shape and the position of the holes. A thicker film is deposited along the sidewall of the shorter axis of the oval pattern than the sidewall of the longer axis at the middle of the holes. However, a thinner film is deposited along the sidewall of the shorter axis at the opening of the holes. This difference of film thickness can be explained by the behavior of sputtered masking materials and the randomly moved polymer radicals. The differently deposited films on the sidewall of the holes result in the deformation of the transferred pattern. Different film thickness at the opening produces the asymmetric local electrical field. The electric field results in bending the ion trajectory to the longer axis. Because of the ion accumulation, the profile in the longer open axis becomes more vertical. Moreover, the thicker film on the sidewall of shorter axis at the middle of the holes prevents from etching the sidewall. Therefore, transferred patterns in the bottom of the holes become more oval shaped than patterns in the masking layer.

PS2-TuP12 Empiric Study on the Effects of Two Different Film Stack Approaches on Gate Etching in Typical High-Density Plasma for Advanced Embedded Logic & Flash Systems*, **S. Sciarrillo,*** STMicroelectronics, Italy

Advanced Embedded logic & flash memory systems (120nm and below) requires necessarily new and complex solutions in terms of process integration. An empiric study on the effects of two different film stack approaches on gate etching in typical high-density plasmas will be discussed in this paper. Profile evolution of a high aspect ratio dense pattern could change in significant way if between photoresist (193nm) and polysilicon a thin oxide layer has (or not) been grown by a previous oxidation. In the top-poly oxidation approach, for the first time, evident notching at the middle height of the structure (not at the bottom as typically known) has been seen; the observed phenomenon depends on the pattern density and the electrical connection status of the polysilicon lines. An extensive morphological analysis has been performed and the results suggest the presence of three correlated effects during the etching: a) electron shading; b) resist bending (depending on the local charging of the neighboring surfaces); c) notching mechanism.@footnote 1@ Dependence on the aspect ratio (different resist thickness) and on the film stack (w/wo top oxidation) has been empirically characterized. A Process window on the different etching steps has permitted to identify the strategy to reduce substantially the morphological issues, e.g. towards a straight gate profile. Achieved results are consistent with the electron shading effect, notching theory and with the relationship between the resist thermo-physical properties (T@sub g@) and its thickness.@footnote 2@ @FootnoteText@ @footnote 1@ R.J. Dhul, S.J. Pearton (Eds.), Handbbok of Advanced Plasma Processing Techniques, Springer Ed., 257-308 (2000)@footnote 2@ N. Vourdas, A.G. Boudouvis, E. Gogolides, Microelectronic Engineering 78-79, 474 (2005)

PS2-TuP13 A Comprehensive Characterization of the Silicon Substrate Surfaces Damaged by Plasma Processes and the Impacts on Future Scaled Devices*, **K. Eriguchi,** K. Nakamura, M. Kamei, D. Hamada, H. Fukumoto, K. Ono,* Kyoto University, Japan

The surfaces of silicon substrates after the plasma exposure have been investigated by primarily using optical techniques; photoreflectance (PR) spectroscopy and spectroscopic ellipsometry. Electron Cyclotron Resonance (ECR) and DC plasma sources with Ar-based gas mixtures were employed to induce the defect generation in the substrates for various biasing conditions, i.e., ion bombardment energies, and process durations. The PR studies with an s-polarized probe beam at the 80° grazing-incidence angle have revealed the decrease in the reflectance change by the plasma exposure, but no significant shift of the optical transition energy at around 3.3-3.4 eV, indicating that the carrier recombination centers are generated in the vicinity of the interface between the natural oxide layer and silicon substrate. The ellipsometric analysis based on the classical dispersion has identified the damaged-layer and determined the thickness as thinner than 6 nm for all the process conditions conducted in this study. The substrate resistivity measurement has shown the increase in the standard deviation of the values by the plasma exposure. The defects in the substrate surface region were further identified distinctly by the present PR setup for the sample treated by the ECR plasma system under no biasing condition (Ar/O@sub 2@ gas mixture). Based on this new finding, we conclude that the thickness and electrical property of the plasma-damaged layer should be taken into account for future scaled devices, e.g., those with the junction depth shallower than 10 nm.

PS2-TuP15 Deposition and Characterization of SiO@sub x@N@sub y@Bottom Anti Reflective Coating (BARC)*, **X. Peng**, Z.Y. Wang, D. Dimtrov, S. Xue,* Seagate Technology

With the shrinking of the critical feature line width in both semiconductor and storage industries to meet the ever-increasing requirement for high package density/recording density, the control of the critical feature dimension at sub 100 nm is a big challenge. The industry trend is using shorter wavelength (193 nm for example) lithography for better resolution and using BARC for minimizing standing wave formation and better CD control. Matching the optical constants (n, k) between the BARC, photo resist and underlayer is critical in eliminating the standing waves. SiO@sub x@N@sub y@ and SiO@sub x@C@sub y@ are two attractive inorganic BARC candidates, due to their adjustable optical constant by varying the deposition parameters and their etching compatibility with standard plasma process. SiO@sub x@N@sub y@ films have been prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD) approach at various process parameters, such as SiH4 flow rate, SiH@sub 4@/N@sub 2@O ratio and NH3 flow rate. SiO@sub x@N@sub y@ films have been characterized using x-ray photoelectron spectroscopy (XPS) for chemical composition depth profile, FTIR for local chemical bonding and ellisometry for optical constants. It has been demonstrated that the refractive index of SiO@sub x@N@sub y@ can be tuned from 1.6 to 2, while k can be adjusted from 0.1 to 0.9. Inductively coupled plasma (ICP) has been used to etch the SiO@sub x@N@sub y@ film for pattern transferring capability study with CHF@sub 3@+O@sub 2@ chemistry. CN emission line at 387 nm wavelength was used for endpoint. The profile of the etched SiO@sub x@N@sub y@ is studied by cross-section transmission electron microscopy (TEM). Finally, the SiO@sub x@N@sub y@ BARC application in combination with hard mask has been discussed

Plasma Science and Technology
Room 3rd Floor Lobby - Session PS3-TuP

Advanced Plasma Deposition Poster Session

PS3-TuP1 Room Temperature Crystallization of Amorphous Thin Films using RF Plasma*, **Y. Shibayama**, M. Suzuki, A. Kinbara, T. Watanabe, H. Ohsaki,* The University of Tokyo, Japan

Crystallization of amorphous thin films was achieved by using a RF plasma treatment. Sol-gel TiO_2 / Si wafer, sputtered ITO / glass and sputtered Si / glass are crystallized by 2 minute-treatment and the sample temperature is lower than 150°C during the plasma treatment. Sol-gel derived TiO_2 films with about 66% packing density was densified to 91% and crystallized into anatase. Plasma-crystallized anatase films show photo-induced super-hydrophilicity and photocatalytic activities while as-coated sol-gel TiO_2 does not indicate such phenomena. Amorphous ITO films were deposited on soda-lime glass with alkali-barrier silica film without substrate heating. Resistivity of ITO films decreased by the plasma treatment and the surface of the ITO films was kept smooth after the treatment. Amorphous Silicon film including a small amount of randomly orientated crystallites were prepared by sputter method and XRD peaks grew by the plasma treatment with keeping the XRD peak height ratios almost the same as ones of polycrystalline Silicon. Amorphous Silicon films with preferred oriented crystallites were also prepared by sputter method. It can be concluded from XRD analyses that the plasma treatment realizes preferential crystal growth. In the presentation, the details of this plasma crystallization technology will be presented.

PS3-TuP2 Formation of Ultra Water-Repellent Thin Films in Organosilane Plasma by PECVD Method*, **Y.S. Yun**, T. Yoshida, N. Shimazu, Y. Inoue, N. Saito, O. Takai,* Nagoya University, Japan

Ultra water-repellent films, inspired by water-repelling lotus leaves, have been attracted over the last few years to both fundamental research and practical applications. We have succeeded in fabricating ultra water-repellent thin films at room temperature by microwave plasma enhanced CVD using organosilicon compounds as raw materials. However, activated reactions in the PECVD process are too complicated to make clear its deposition mechanism. In this study, we investigated reactions in organosilane plasma by using optical emission spectroscopy and mass spectrometry in order to understand the formation reaction of ultra water-repellent thin films in the PECVD process. Surface morphology, chemical composition and bonding states of the films were analyzed. From the results, we found that there are several stages in formation of ultra water repellent thin films. That is, at the first stage of the growth, the nano-clusters seem to fall randomly on the surface. These clusters probably originate from a polymerization process in the gas phase and deposit on the substrate. When the film was deposited for several tens of seconds, the nano-clusters show a tendency to form chains or islands, which means the clusters must have a spatial preference. Finally, these films have particular nano-textures with nano-scale pores of a few hundreds nanometer in size among the cancellous web-like structure of the nano-cluster agglomerates. The rough surface of the films results in the water contact angles greater than 150 degree.

PS3-TuP3 Controlling the Fluxes of Carbon Supply for Carbon Nanotube Growth in CH_4/H_2 Plasma*, **A. Okita**, Y. Suda, A. Ozeki,* Hokkaido University, Japan*; A. Oda,* Nagoya Institute of Technology, Japan*; J. Nakamura,* Tsukuba University, Japan*; K. Bhattacharyya, H. Sugawara, Y. Sakai,* Hokkaido University, Japan

Carbon nanotubes (CNTs) exhibit unique properties such as high chemical stability and current density. We are interested in LSI applications of CNTs utilizing their electronic properties. However, LSI technology demands the precisely control of CNTs growth with regard to placement, length, diameter and number density. We have focused on the growth speed of CNTs in order to fulfill the above demands. The purpose of this paper is to investigate the growth speed of CNTs by controlling the fluxes of carbon source. We have used plasma-enhanced chemical vapor deposition (PECVD) for CNT growth.[1] PECVD can effectively decompose gas molecules and produce the precursors for CNTs such as ions and radicals. In this experiment, $Al_2O_3/Fe/Al_2O_3$ (1/1/1 nm) thin films were used as catalyst (Fe)/support (Al_2O_3) materials, and vertically-aligned CNTs were obtained using CH_4/H_2 plasma. The degree of catalyst activities and oxidation states were observed by X-ray photoelectron spectroscopy (XPS), and CNTs obtained were evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).[1,2] In addition, CH_4/H_2 plasma was simulated by one-dimensional fluid model to analyze the correlation with the CNTs growth and plasma gas phase.[1] This simulation results correlating to experimental condition enable us to predict the fluxes of carbon-containing species onto the substrate. As the results, average length of CNTs became shorter by applying positive DC bias to the substrate. We will discuss the effect of bias voltage on CNT growth speed and compare the simulation results in terms of the difference of fluxes of carbon-containing species.

[1] A. Okita, et al., J. Appl. Phys. 99 (2006) 014302, [2] A. Okita, et al., Jpn. J. Appl. Phys., (accepted).

PS3-TuP4 Pulsed PECVD Processes with E-beam Generated Plasmas*, **D. Leonhardt**, S.G. Walton,* US Naval Research Laboratory

Plasma enhanced chemical vapor deposition (PECVD) processes open up wide parameter spaces (most notably lower substrate temperatures) than CVD techniques. This is because the plasma electrons can directly impart energy into the gas species on the order of 1 eV (> 10,000 K) instead of relying on strictly thermal surface processes. Modulated plasmas in turn can provide even greater control over the deposition conditions by tailoring a gas/surface phase synergy to achieve optimum growth conditions for the desired films. This work will discuss recent progress on PECVD of Si-based films using pulsed electron beam generated plasmas with organic precursors such as TEOS and HMDSO. In these systems, pulse lengths were varied from below 1 millisecond to multiple milliseconds to determine the effects of less total power being imparted to the plasma and gas constituents. Shorter pulse lengths, comparable to gas and surface phase reaction times were expected to have a significant effect on the process deposition rate and the final film quality. These film characteristics will be discussed and compared with complementary time-resolved ion flux measurements (in situ mass spectrometry) and global plasma parameters (from electrostatic probes). Films compositions were varied from SiO_x, SiN_x, and polymeric Si-O complexes, tailored for display applications on flexible substrates (low temperature, low damage) and large area capacitor fabrication.

This work supported by the Office of Naval Research.

PS3-TuP5 Diagnostics of Microwave Plasmas Applied for Organic Layer Deposition*, **S.F. Dribinskiy**, G. Franz,* Munich University of Applied Sciences, Germany*; D. Voss,* Plasma-Parylene Coating Services, Germany

Polyparylene, a non-critical, non-toxic layer material for long-term applications in the human body, has been deposited by plasma-enhanced chemical vapor deposition of the monomeric species. For that end, a microwave discharge in a pulsed mode has been applied. Important plasma parameters have been evaluated by simultaneous application of Langmuir probe and trace rare gas optical emission spectroscopy. Plasma densities and electron temperature have been found to cover values from an almost dark Langmuir plasma up to $10^{10}/cm^3$ and between 1 and 3.5 eV, respectively. Differences in electron temperature between the two methods were less than 20 %. Due to the skin effect which is already effective beyond plasma densities of some $10^9/cm^3$, the plasma is spatially inhomogenous which has been taken care of by measuring at three different positions with the Langmuir probe. Entering from the radially outmost position, the inverted V-shape profiles for plasma density and electron temperature peak in the border reagion. This holds true for argon and parylene. However, the plasma density in parylene is lower by a factor of nearly 10 indicating that this molecule and/or its fragments exhibit a strong power for electronic attachment. The skin effect is also responsible for the decreasing plasma density with growing discharge pressure. Finally, the decay constant has been determined and modeled.

PS3-TuP6 Behavior Analysis of Various Organosilicon Molecules in PECVD Processes*, **T. Yoshida**, Y.S. Yun, N. Shimazu, Y. Inoue, N. Saito, O. Takai,* Nagoya University, Japan

Plasma enhanced chemical vapor deposition (PECVD) using organosilicon reactants are one of the most promising deposition processes because of its ability to prepare several functional films such as low-k films for semiconductor devices and ultra water-repellent coatings.ã??Although large number of studies has been made on the relations between film properties and functions, fewer studies has been devoted to the plasma itself. Therefore, the behavior of organosilicon molecules in PECVD processes has been poorly understood. To control the film property, it is absolutely imperative to clarify the behavior of organosilicon molecules. In this study, we investigate the behavior of reactant organosilicon molecules in plasma by means of Optical emission spectroscopy (OES), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy

(XPS) and other analysis. The hydrocarbon-doped silicon oxide films were prepared with an inductively-coupled rf PECVD system. Trimethylmethoxysilane (TMMOS), hexamethyldisiloxane (HMDSO) and hexamethylcyclotrisiloxane (HMCTS) are used as reactants. Si(100) substrates were kept at around room temperature during deposition. The OES of HMDSO and HMCTS plasmas were very similar and are dominated by H, H2 and CH emissions. On the other hand, we could observe not only H, H2 and CH but also CO and OH emissions in TMMOS plasma. It propose that the oxygen atoms of methoxy groups in TMMOS molecules can be dissociated easily in the plasma and behave as a kind of oxidizing agent whereas siloxane bondings in HMDSO and HMCTS are hardly expel oxygen atoms.

PS3-TuP7 Amorphous Carbon Coating Mixed with Nano Crystalline Diamonds*, **N. Sakudo**, N. Ikenaga, Y. Tashiro, A. Sakamoto,* Kanazawa Institute of Technology, Japan

We have developed new carbonic coating that can be applied to machine tools and dies. The coating, which we named hybrid nano-diamond coating, consists of multi layers with nano crystalline diamonds and amorphous carbon that is so-called DLC (diamond like carbon). Usually pure diamond coating had been carried out at a high substrate temperature of around 1000 K by microwave plasma CVD (chemical vapor deposition) using methane diluted with hydrogen. On the other hand, pure DLC coating had been carried out at a lower substrate temperature than 500 K by PVD (physical vapor deposition) using hydrocarbon gases like ethylene, ethane, acetylene and so on. In order to make the new carbonic coating on low temperature substrate, we constructed an apparatus that has two different plasma generators. One is a 2.45 GHz microwave-plasma source with slotted rectangular waveguide surrounding the plasma chamber, and the other is an inductively-coupled plasma source with one-turn loop antenna driven by 13.56 MHz RF power. The microwave plasma is used for nano diamonds and RF plasma for DLC, respectively. The substrate temperature can be kept lower than 500K during the whole process. The coating was applied to cutting-tool chips for a milling machine and the tool life was tested by machining aluminum alloys. In comparison with conventional DLC coating, the hybrid nano diamond coating showed longer life.

PS3-TuP8 Polymer Surface Modification using Electron Beam-Generated Plasmas*, **S.G. Walton**, D. Leonhardt,* US Naval Research Laboratory

Electron beam-generated plasmas have several unique characteristics that make them attractive for polymer modification or other processing applications where substrate material sensitivity is an issue. The US Naval Research Laboratory has developed a plasma processing system that relies on a magnetically collimated, sheet of multi-kilovolt electrons to ionize the background gas and produce a planar plasma. High-energy electron beams are efficient at producing high-density plasmas ($n_e > 10^{11}$ cm^{-3}) with low electron temperatures ($T_e < 0.5$ eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 3 eV) at surfaces located adjacent to the electron beam. Most relevant to the processing of sensitive materials is the ability of these sources to provide large fluxes of reactive species and limiting ion kinetic energies to values near common bond strengths, all of which is achieved under low pressure operating conditions and small source-to-substrate distances. In this work, we discuss the processing of common polymers such as polyethylene using pulsed, electron beam-generated plasmas produced in pure argon and mixtures containing reactive gases such as SF_6 and O_2. This work focuses on tailoring the surface energy while minimizing substrate damage. Plasma diagnostics used to provide a more complete understanding of the system are also presented. We include the processing of porous polymer substrates using a dual source system specifically designed for the treatment of thin, porous or fibrous sheets. This work was supported by the Office of Naval Research.

PS3-TuP9 Chemical Modification of the Poly(Vinylidene Fluoride-Trifluoroethylene) Surface through Fluorocarbon Ion Beam Deposition*, **W.-D. Hsu**, I. Jang, S.B. Sinnott,* University of Florida

Classical molecular dynamics simulations are used to study the effects of continuous fluorocarbon (FC) ion beam deposition on a poly(vinylidene fluoride-trifluoroethylene), P(VDF-trFE), surface. Fluorocarbon plasma processing is 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. The deposition of mass selected fluorocarbon ions is useful to isolate the effects specific to polyatomic ions. This research focuses on the differences in the chemical interactions of $C_3F_5^+$ ions and CF_3^+ ions with P(VDF-trFE) surface. The incident energy of the ion beams is 50 eV/ion. The CF_3^+ ions are predicted to be more effective at fluorinating the P(VDF-trFE) surface than $C_3F_5^+$ ions. At the same time, the $C_3F_5^+$ ions are predicted to be more effective in growth of fluorocarbon thin film. The simulations also reveal possible mechanisms that could produce these differences, which will be discussed. This work is supported by the National Science Foundation (Grant number CHE-0200838).

PS3-TuP11 Atmospheric Plasma Deposition of Silicon Dioxide Coatings on Metal*, **A.M. Ladwig**,* University of California - Los Angeles*; S.E. Babayan,* Surfx Technologies*; M.D. Smith, W. Highland,* National Nuclear Security Administration's Kansas City Plant Operated by Honeywell Federal Manufacturing and Technologies*; R.F. Hicks,* University of California - Los Angeles

The deposition and properties of silicon dioxide on metal substrates was investigated using atmospheric pressure plasma-enhanced chemical vapor deposition. The plasma, generated with radio frequency power at 27.12 MHz, was fed helium, oxygen and two types of silicon precursors, hexamethyldisilizane and tetraethylorthosilicate. After deposition, the films were analyzed for composition, adhesion and dielectric strength. X-ray photoelectron spectroscopy revealed that the glass films contained approximately 25 percent silicon, 50 percent oxygen and 25 percent carbon with negligible nitrogen. Scratch tests indicated that the films were strongly adherent to the substrates. The glass films achieved direct current dielectric strengths between 50 and 250 V for a thickness range of 0.5 to 1.3 µm. The maximum breakdown voltage measured was 400 V. Scanning electron microscopy revealed that breakdown occurred at cracks and other defects in the films. These defects appeared to form around areas of surface roughness and contamination. The process conditions and their effects on the properties of silicon dioxide will be presented.

PS3-TuP12 Properties of Various Polyparylenes Deposited by Conventional and Plasma-Enhanced Chemical Vapour Deposition*, **G. Franz**, S.F. Dribinskiy,* Munich University of Applied Sciences, Germany*; D. Voss,* Plasma-Parylene Coating Services, Germany

Polyparylene, a non-critical, non-toxic layer material for long-term applications in the human body but also a very promising candidate for a low-κ dielectric, has been deposited by conventional and plasma-enhanced chemical vapor deposition of the monomeric species (types C and N), and partly with CF_4. For that end, a microwave discharge in a pulsed mode has been applied. The characterization of the layer parameters has been compared with conventionally prepared cvd data. The analytical tools were scanning electron microscopy and atomic force microscopy to determine the surface roughness and density of voids in the film; the surface tension has been evaluated by contact angle measurements and the high-frequency dielectric constant by ellipsometry. Fourier-transform infrared spectroscopy served to define the occurrence of functional groups. The most prominent detail is the contact angle against water and the organic solvent CH_2I_2 which varies between very flat angles up to nearly 180° so it is possible to fabricate plasma-generated films which simultaneously exhibit hydrophobic and lipophobic character. Conventionally produced films, however, are more or less hydrophobic. Together with the very smooth surface which nearly completely lacks voids, we refer this conduct partly by physical reasons: the higher energy of the layer-composing molecules in the plasma case. In a chemical sense, this behavior is caused by the almost complete destruction of the benzene ring even in a relatively gentle plasma. Eventually, the tribological and dielectric film properties are correlated with the deposition conditions.

PS3-TuP13 Plasma and Surface Characterisation in the Pulsed Polymerisation of Acrylic Acid Films*, **J.W. Bradley**, S. Voronin,* University of Liverpool, UK*; M.R. Alexander,* University of Nottingham, UK

The pulsed-plasma polymerization of functional films from organic monomers struck at low pressure in RF discharge cells is a valuable technique for controlling surface chemistry and obtaining good functional retention.[1] Despite the usefulness of the pulsed plasma technique, the relationship between the transient plasma parameters during the pulse cycle (typically several milliseconds duration) and the chemical and physical properties of the film has not been extensively investigated. Using state-of-the-art time-resolved mass spectroscopic and electrical probing techniques, the plasma parameters, (neutral and ion flux, ion energy distribution function, plasma density, electron temperature and plasma potential) have been measured in a range of monomer flow rate to applied power ratios and pulse duty cycles and correlated with the surface

chemistry obtained by XPS. We have evidence for the importance of heavy ionic species (e.g. $[xM\text{-}H]^{+}$ with x = 2, 3) originating from the plasma in the production of high functional retention films. A growth model for pulsed-plasma polymer films is being developed. @FootnoteText@ @footnote 1@ Rinsch CL, Chen XL, Panchalingam V, Eberhart RC, Wang JH, Timmons RB, Langmuir 12 (12) 2995-3002 1996

PS3-TuP15 Nanopantography: A New Approach for Massively Parallel Fabrication of Nano-Structures*, **M.K. Jain,** L. Xu, S.C. Vemula, S.K. Nam, V.M. Donnelly, D.J. Economou, P. Ruchhoeft,* University of Houston

Nanopantography is a new method for forming nano-structures on a massively parallel scale. A nearly monoenergetic ion beam (FWHM < 3 eV at 100 eV) is directed at a 3-layer (Cr/SiO_2/Si substrate) electrostatic lens structure built on a silicon wafer. A typical lens consists of a micron size hole etched through the metal and oxide layers down to the Si substrate. When the optimum potential is imposed on the metal layer, the ion "beamlets" entering the 1 µ hole openings focus to 10 nm size spots. Optimum potentials were obtained by ion trajectory simulations. Etching or deposition on the Si substrate can be accomplished depending on the choice of ions and effusive neutral beams. We performed etching experiments with 100 eV Ar^{+} ions, formed in a pulsed ICP, and a Cl_2 effusive beam, and etched 10nm dia., 100 nm deep holes in Si with 950nm dia. lenses. When the sample was tilted 20° off normal with respect to the ion beam axis, the focused spot moved by 160nm off axis, in agreement with simulations. Thus, sample tilting will enable us to write lines and complex patterns with nanometer resolution. Deposition of ~50 nm dia. Ni islands was also accomplished with 20 eV Ni^{+} ions formed by sputtering of a Ni target in the pulsed ICP.

Plasma Science and Technology
Room 2009 - Session PS1-WeM
Plasma-Surface Interactions II

Moderator: V.M. Donnelly, University of Houston

8:00am **PS1-WeM1 Carbon Exposed to Hydrogen Plasma of ITER Relevant Conditions in Pilot-PSI**, ***G.J. van Rooij***, *W.A.J. Vijvers, J. Westerhout, H.J.N. van Eck, W.R. Koppers, V. Veremiyenko, W.J. Goedheer, B. de Groot, P. Smeets,* FOM-Inst. for Plasma Phys., The Netherlands*; R. Engeln, D.C. Schram,* Eindhoven Univ. of Tech., The Netherlands*; H.J. van der Meiden, N.J. Lopes Cardozo, A.W. Kleyn,* FOM-Inst. for Plasma Phys., The Netherlands

Plasma surface interaction (PSI) in the divertor of ITER and fusion reactors beyond ITER, is a critical research area in the development of fusion power. For ITER, power and particle flux densities of 10 MW/m@super 2@ and 1E24 m@super -2@s@super -1@ respectively are foreseen, at ne < 1E21 m@super -3@ and Te in the few eV range. Pilot-PSI is a linear plasma generator that studies the production of such plasma conditions with a cascaded arc in magnetic fields up to 1.6 T. These studies are required for the design of the larger linear plasma generator Magnum-psi (Magnetized Plasma Generator and Numerical Modelling for Plasma-Surface Interactions Studies), which is being build by FOM in collaboration with ist TEC partners to address the physics of PSI in this extreme regime. In this contribution, we show on the basis of Thomson scattering and optical emission spectroscopy results that the specified plasma parameters have been realized in Pilot-PSI. We demonstrate how the geometrical details and the operation parameters of the cascaded arc can be optimized for high hydrogen plasma yields in strong magnetic fields. This knowledge is used to produce the record numers of ne = 5E21 m@super -3@ and Te = 5 eV. Pilot-PSI is already a unique experiment for the field of PSI-studies on the basis of these numbers. In preparation for detailed PSI studies on the hydrogen plasma and carbon surface system, we have performed preliminary experiments by exposing carbon targets to the Pilot-PSI plasma jet. The carbon content in the plasma was monitored in these experiments with optical emission spectroscopy on the CH band and the Balmer @gamma@ line. In addition, Cavity Ringdown Spectroscopy was installed for characterisation of the plasma close to the surface. Results will be shown on the detection of CH (around 431 nm) and C2 (around 517 nm). The effect of the exposure on the target was analysed off line by means of the XPS instrument that is available within our PSI-lab.

8:40am **PS1-WeM3 Control of Atomic Layer Degradation on Si Substrate**, *T. Tatsumi,* Sony Corporation, Japan*;* ***Y. Nakamura****, T. Harano,* Sony Semiconductor Kyushu Corporation, Japan*; K. Kugimiya,* Sony Corporation, Japan*; T. Kawase, S. Hamaguchi,* Osaka University, Japan*; S. Iseda,* Sony Semiconductor Kyushu Corporation, Japan

To suppress the fluctuation of transistor properties, the degradation on Si substrate must be minimized. We quantitatively evaluated the relationship between ion energy at high energy peak of IEDF, the thickness of a C-F polymer (T@sub C-F@), and the thickness of damage (T@sub d@) formed during the etching of SiO@sub 2@ on an Si substrate. CH@sub 2@F@sub 2@/CF@sub 4@/Ar/O@sub 2@ plasma was used for experiments. The T@sub d@ were evaluated using XPS, TEM, and RBS. The changes of surface layers in the early stage of damage formation were estimated using molecular dynamics (MD) simulations. By increasing the O/CF@sub 2@ ratio in the plasma, T@sub C-F@ decreased, and T@sub d@ was a minimum under conditions where the penetration depth of ions (T@sub ion@) was equal to T@sub C-F@ (the balance point: P@sub b@). When O/CF@sub 2@ > P@sub b@, T@sub d@ increased when T@sub C-F@ decreased because the ion energy consumption by the polymer was smaller. On the other hand, when O/CF@sub 2@ was less than P@sub b@, T@sub C-F@ increased with time, and T@sub d@ increased when the rate at which the polymer was deposited was increased. We used MD simulations to evaluate the surface around the transition from SiO@sub 2@ etching to Si etching. Damage started forming just before the SiO@sub 2@ was completely removed, and when the SiO@sub 2@ was etched off, the highest T@sub d@ was observed. Then, T@sub C-F@ began to increase, and T@sub d@ slightly decreased by desorbing unstable SiC@sub x@F@sub y@ species. When T@sub C-F@ became larger than T@sub ion@, the damaged layer was buried, and changes in T@sub d@ stopped. T@sub d@ can only decrease until T@sub C-F@ reaches the ion penetration depth. We carefully adjusted T@sub ion@ to be equal to T@sub C-F@ under low ion energy conditions; T@sub d@ was reduced to below 1 nm. Thus, the precise control of ion energy and the prediction of several atomic layers on an actual etched surface will be indispensable in the fabrication of 32nm-node devices.

9:00am **PS1-WeM4 Modifications of Advanced Photoresist Polymers after Plasma Processing**, ***S. Engelmann****, R.L. Bruce, B.F. Smith, T. Kwon, R. Phaneuf, G.S. Oehrlein,* Univ. of Maryland College Park*; C. Andes,* Rohm & Haas Electronic Materials*; D.B. Graves, D.G. Nest, M. Goldman,* UC, Berkeley*; E.A. Hudson,* Lam Research Corp.*; P. Lazzeri, E. Iacob, M. Anderle,* ITC-irst, Center for Sci. and Tech. Res., Italy

Plasma based transfer of photoresist patterns onto underlying substrates is basic to micro- and nano-fabrication, but suffers from problems like introduction of surface and line edge roughness in the photoresist/underlying features as a result of plasma processing. In this collaboration, we seek to develop a deeper understanding of this behavior along with the formulation of design criteria for new photoresist systems. Etch rates, chemical and morphological evolution of fully formulated photoresist systems as well as carefully selected model polymers have been studied using Ellipsometry, Atomic Force Microscopy, Time-of-Flight Secondary Ion Mass Spectrometry and X-Ray Photoelectron Spectroscopy. We find that the polymer structure in the top surface layer is destroyed within the first 2-3 seconds of plasma exposure accompanied by hydrogen-loss and densification. Furthermore we observed a strong correlation between polymer structure, plasma-induced surface chemistry, and morphological evolution of the sample. We also observed that acrylate content improves the etch performance of our materials and that the plasma etching rate and surface roughening of a fully formulated photoresist is essentially the same as that of the polymer backbone of which it consists. Varying the physical properties of the plasma attack can greatly modify these chemical and morphological changes. The role of process chemistries as well as the effect of ion energy or ion/neutral ratio and the effect of materials modifications for selected conditions will be addressed.

9:20am **PS1-WeM5 Study of Energetic Ion and Radical Beams Interacting with Advanced Photoresist Polymers**, ***D.G. Nest****, M. Goldman, D.B. Graves,* UC Berkeley*; S. Engelmann, R.L. Bruce, B.F. Smith, T. Kwon, R. Phaneuf, G.S. Oehrlein,* Univ. of Maryland*; C. Andes,* Rohn and Haas Electronic Materials*; E.A. Hudson,* Lam Research Corp.*; P. Lazzeri, M. Anderle,* ITC-Irst, Italy

The effects of ions and radicals in plasmas on current and future photoresists (PR) are poorly understood, even though PR degradation is known to be an increasingly important problem for micro- and nano-fabrication. We report results from a collaborative study of etching and roughening mechanisms on fully formulated methacrylate-based 193 nm photoresists as well as on model polymers that make up the fully formulated compounds. We measure the effects of beams of ions and radicals impacting selected materials in vacuum to simulate plasma-photoresist interactions under controlled conditions. We highlight the importance of rare gas ion energy and mass and surface temperature on surface roughening and etching, both with and without chemical effects associated with radical impact. For example, Ar@super +@ impact at normal incidence and 1 keV results in a smooth PR surface, but 300 eV ion impact steadily roughens the surface. Surfaces impacted by Ar@super +@ at normal incidence and 500 eV are smooth at 25°C but steadily roughen at surface temperatures above about 40°C. Results of ion sputtering of patterned contact holes and trenches will be presented. Results are compared to measurements in plasmas where possible.

9:40am **PS1-WeM6 Investigation of Plasma-Polymer Interactions for Plasma/Energetic Beam Templating of Materials**, ***R.L. Bruce****, C. Dutton, G.S. Oehrlein, S. Engelmann, T. Kwon, R. Phaneuf,* Univ. of Maryland, College Park*; B. Long, G. Willson,* Univ. of Texas, Austin*; D.B. Graves, D.G. Nest, J. Vegh,* UC, Berkeley*; A. Alizadeh,* GE Electrics Global Research Center

Plasma processing of nanoscale patterned organic masks can lead to surface and line edge roughening and can also lead to changes in dimensions and properties of completed nanostructures for reasons that are not well understood. Using an inductively coupled plasma chamber, tailored polymers were processed in well-characterized controlled plasmas (O@sub2@, Ar, Ar/C@sub4@F@sub8@) and then analyzed using a number of characterization tools: ellipsometry, atomic force microscopy, Fourier-transform infrared spectroscopy, and x-ray photoelectron spectroscopy. Similar polymers (polystyrene, poly(alpha-methylstyrene), poly(para-methylstyrene)) exposed to the same plasma conditions were found to behave very differently in etch yield, rms roughness, and refractive index evolution. Characterization of chemical bonding and

composition in the damaged layer of these polymers by x-ray photoelectron spectroscopy and infrared spectroscopy give insights into the different plasma-polymer interactions in similar polymers. We discuss the different behavior of the polymers in the plasma environment in terms of fundamentally different responses to radiation environments, including cross-linking and scission.

10:40am **PS1-WeM9 Molecular Dynamics Simulations of Interactions of Ions and Radicals with Organic Masking Materials**, ***J.J. Végh**, D.G. Nest, M. Goldman, D.B. Graves,* University of California at Berkeley*; R.L. Bruce, S. Engelmann, T. Kwon, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park*; B. Long, G. Willson,* University of Texas, Austin*; A. Alizadeh,* GE Electric Global Research Center

Plasma-organic polymer surface interactions are important in etching, deposition, surface treatment and modification. Organic polymers are used as etch masks in both conventional photoresists and in novel masking schemes such as imprint lithography and self-assembled block copolymer masks, but the mechanisms of etching are poorly understood. We describe studies of ion and radical impacts on organic polymer surfaces using molecular dynamics (MD) simulations, focusing on etch mechanisms for model polymers such as polystyrene. Experiments have revealed that polymers, including commercial photoresists, initially experience a rapid, drastic reduction in sputtering yield before reaching a much lower steady state value. The MD simulations reproduce this drop in sputtering yield, and are also able to predict the ion fluence necessary to reach steady state. Simulations reveal that the near-surface region becomes hydrogen-depleted with Ar@super +@ bombardment, leading to an amorphous carbon layer that reduces the sputtering yield by as much as two orders of magnitude. We present further results explaining polymer etch in the presence of F and CF with Ar@super +@ bombardment, contrasting polymer etch mechanisms with those of materials such as silicon. Results are compared with energetic beam and plasma experimental measurements.

11:00am **PS1-WeM10 Scattering Dynamics of Fluorinated Ions on Surfaces of Relevance to Plasma Etching**, ***M.J. Gordon***, LTM/CNRS, France*; X. Qin, J. Mace, K.P. Giapis,* California Institute of Technology

Fluorocarbon plasmas are extensively used for SC, dielectric, and metal etching; in particular, F-based etching of Si has been studied for many years. However, little is known about specific interactions (kinematics/charge exchange/reaction dynamics) of F-containing ions at collision energies relevant to plasma processing (0.1-1 keV). This talk will focus on experiments involving mass-filtered ions (F+, CFx+) with tunable energy (50-1000 eV) and high flux scattered off a variety of surfaces. Beam studies were carried out in an ICP-based accelerator system with simultaneous energy/mass analysis of products leaving the target. We first highlight two new effects in the F+-Si/Al systems: electronic excitation during the hard collision to form inelastic F+/F2+ and stimulated desorption of hyperthermal (10-20 eV) F+ (HT-F+). Inelastic losses and F2+ were attributed to the formation of doubly-excited autoionizing states of F and F+ (analogous to Ne) in the hard collision. HT-F+ is thought to originate from core-hole charge transfer involving a surface-bound F atom. These two effects are potentially important for profile evolution because F+ scattering becomes inelastic at low collision energies (300/500 eV for Al/Si) and desorbing HT-F+ may enhance the reactivity at surfaces not accessible to plasma ions. In the second part of the talk, collision kinematics of CFx+ ions off Si and metals will be discussed. Velocity analysis of scattered fragments suggests that neutralization induced dissociation of the projectile occurs before the hard collision (CF3+ is neutralized on approach and dissociates to form CF or CF2). The resulting CF/CF2 fragments then scatter elastically off the surface to form a hot positive ion, which dissociates to F+C or F+CF, with both fragments leaving at similar velocities. This reaction scheme was seen to depend on both the incident energy and target material. Implications of these findings for plasma etching and profile evolution will be discussed.

11:20am **PS1-WeM11 Plasma-Surface Interactions During Deposition of Hard Carbon Materials**, *D. Liu, J.M. Stillhan, **E.R. Fisher**,* Colorado State University

Hard carbon-based materials such as carbon nitride and diamond-like carbon (DLC) have many desirable properties such as high hardness, good thermal conductivity, and high electrical resistance. Although plasma deposition and etching of these materials has been widely studied, very little has been reported on gas-phase ion and electron kinetics in these systems and even less is available on plasma-surface interactions. We have performed Langmuir probe and energy analysis-based mass spectrometry measurements to characterize the gas-phase of low pressure, 13.56 MHz inductively coupled plasma molecular beams. In addition, hydrogenated DLC and a-C:N films were deposited on silicon wafers at different substrate potentials to determine the effect of ion bombardment on film properties. Films were characterized via FTIR, SEM, AFM and nanoindentation measurements, and results demonstrate that ion energy has a significant effect on the composition and morphology of plasma deposited DLC films. Most importantly, we have used our unique imaging of radicals interacting with surfaces (IRIS) technique to directly examine surface interactions of radicals during plasma deposition. IRIS data for CH and C@sub 2@ radicals in hydrocarbon plasmas and CH, CN, NH, and NH@sub 2@ radicals in a-C:N deposition systems will be presented. These species display very different surface reactivity that is dependent on plasma parameters, feed gases, and the electronic configuration of the molecule. For example, CH and CN are highly reactive during a-C:N deposition, whereas C@sub 2@, NH and NH@sub 2@ display intermediate reactivity that is highly dependent on substrate bias. IRIS results will be correlated to gas-phase and surface analysis data to provide more comprehensive mechanisms for hard carbon deposition systems.

11:40am **PS1-WeM12 In Situ Surface Diagnostics during Room Temperature Plasma Deposition of Polycrystalline Si Films**, ***E.S. Aydil***, University of Minnesota*; R.C. Mani,* Applied Materials

The ability to deposit crystalline silicon at room temperature would be very attractive for a variety of applications. Crystalline silicon films are obtained when silane is highly diluted in hydrogen, or under conditions where silane is highly dissociated such that there is high concentration of H in the gas phase. In fact, amorphous silicon films undergo disorder-to-order transition upon exposure to H atoms created by plasma dissociation of hydrogen. The mechanism of this disorder-to-order transition was uncovered recently; specifically, it was shown that hydrogen inserts into the strained bonds Si-Si bonds in amorphous silicon, and induces bond-breaking and bond re-forming reactions, which eventually lead to nucleation of crystalline silicon. This chemically-induced crystallization of silicon occurs in the temperature 150-300 C range. However, despite extensive experimental studies, unambiguous room temperature nucleation and growth of microcrystaline Si has not been demonstrated. We demonstrate the deposition of thin films containing nanocrystals of silicon using an inductively coupled plasma source and silane diluted in hydrogen at room temperature. In situ attenuated total internal reflection - Fourier transform infrared spectroscopy and in situ spectroscopic ellipsometry were used to monitor the film structure, temperature and thickness during deposition. The films were also characterized using ex-situ techniques such as Raman spectroscopy and TEM. Both in situ and ex-situ characterization techniques clearly indicated the presence of crystalline domains in the deposited films. In situ spectroscopic ellipsometry revealed that Si nanocrystals nucleate in the bulk and grow beneath an amorphous silicon crust validating the theory of hydrogen-induced crystallization. Crystals as large as 100-150 nm were observed at room temperature. Thus, silicon nanocrystals not only nucleate but also grow substantially in the bulk at room temperature.

12:00pm **PS1-WeM13 In-situ Spectroscopic and Kelvin Probe Studies of the Modification of Passive Films on Metals in Low Temperature Plasmas**, ***M. Giza**, T. Titz, G. Grundmeier,* Max-Planck-Institut fuer Eisenforschung, Germany

Low temperature plasma processes are of increasing interest for the surface modification of engineering metals such as iron, zinc, aluminium, copper or titanium. Many studies have been devoted to the deposition of thin protective, adhesion promoting or biocompatible films on these metal substrates. However, less attention was paid to the influence of the plasma treatment on the passive films between the metal and the deposited plasma polymer. Since the adhesive properties as well as the corrosion behaviour of metals strongly depend on the chemical composition, morphology and electronic structure of their oxides, it is of high interest to reveal principle processes of oxide modification on metals in reducing and oxidising plasmas. Moreover, the question arises how stable these modified oxides are in contact with the underlying metal and with the environment. To answer these questions in-situ analytical set-ups have been designed that allow studies of the plasma modification as well as ageing processes of modified oxides in defined environments. An in-situ set-up for vacuum and atmospheric plasma studies combines a quartz crystal microbalance, FTIR spectroscopy under grazing incidence and a Kelvin Probe.@footnote 1@ For studies in ultra high vacuum an in-situ cell was developed that consists of Auger Spectroscopy in combination with a Kelvin Probe. This plasma cell is connected to an UHV system with ToF-SIMS, XPS and STM. The presentation will cover principle aspects of

relevant passive film structures, the introduction of the in-situ analytical set-ups, oxide modification in vacuum and atmospheric plasmas, the stability of these modified oxides and finally the relevance of the oxide modification for aspects of polymer/metal adhesion and corrosion. @FootnoteText@ @footnote 1@ Raacke, J., Giza, M., and Grundmeier, G., Surface and Coatings Technology, 2005. 200(1-4): p. 280-283.

Plasma Science and Technology
Room 2011 - Session PS2+TF-WeM
Plasma Deposition

Moderator: D. Leonhardt, US Naval Research Laboratory

8:00am **PS2+TF-WeM1 Beam Activation for Atomic Layer Deposition of Ta-Based Barriers on Low-k Dielectric Surfaces**, ***P.S. Ho,*** The University of Texas at Austin*; J. Liu,* The University of Texas at Austin (presently: Tokyo Electron America Inc.)*; J. Bao, H. Shi,* The University of Texas at Austin **INVITED**

Atomic nitrogen and hydrogen beams were investigated as surface pre-treatment and process enhancement techniques for atomic layer deposition (ALD) of tantalum nitride barrier layer on low k dielectric surfaces. Electron cyclotron resonance (ECR) plasma induced atomic nitrogen and hydrogen species were applied to a methyl silsesquioxane (MSQ) and organic polymer low k surfaces prior to and during ALD growth. In-situ XPS studies of the evolution of the low k surface chemistry revealed an initial transient growth region controlled mainly by the substrate surface chemistry. For MSQ surfaces, pre-treatment with atomic beams, particularly with nitrogen atoms, was found to enhance significantly the chemisorption of the TaCl5 precursor on the low k surface. The enhancement was attributed to the dissociation of the weakly bonded methyl groups from the MSQ surface followed by nitridation with the atomic nitrogen species. For the organic polymer surface, the initial interaction was manifested by the formation of a charge transfer complex as a result of the interaction between Ta and the aromatic structure. In the subsequent linear growth region, atomic hydrogen species was able to reduce the chlorine content under appropriate temperature and with sufficient purge. The application of beam activation for pore sealing on porous low k surface will also be discussed.

8:40am **PS2+TF-WeM3 PECVD Synthesis and Optimization of High @kappa@ Dielectric Structures**, *W. Yang, M. Seman,* ***C.A. Wolden,*** Colorado School of Mines

Alternative dielectrics with high dielectric constants (@kappa@) are required to reduce turn-on voltage and leakage current in conventional as well as thin film transistor technology. The latter application requires processing routes with a low thermal budget. To that end plasma-enhanced chemical vapor deposition processes were developed to fabricate high @kappa@ dielectrics including TiO@sub 2@ and Ta@sub 2@O@sub 5@. The deposition rate was found to be weakly activated, enabling low temperature deposition. The deposition rate was a strong function of the atomic oxygen density, reflecting a competition between plasma-phase oxidation of the precursor and its participation in film growth. Metal-insulator-silicon (MIS) structures were fabricated and characterized using both C-V and I-V measurements. Annealing was found to both enhance @kappa@ and significantly attenuate the leakage current. Under optimized conditions the dielectric performance of MIS devices was superior to that of SiO@sub 2@ control samples with the same equivalent oxide thickness. The leakage current density was correlated to the presence of oxide charge defects in the dielectric, as measured using the flat band voltage shift. By appropriate control of plasma power and oxygen concentration, the flat band voltage shift was minimized and the electrical performance of as-deposited films approached those of annealed samples.

9:00am **PS2+TF-WeM4 Tantalum Oxy-nitride Film Deposition by Electron Cyclotron Resonance Plasma Sputtering for MIM Capacitor**, ***T. Ono,*** *H. Toyota,* Hirosaki University, Japan*; M. Shimada, Y. Jin,* NTT MI Labs, Japan

A high-k dielectric film is one of the key to realize high performance large scale integrated circuits (LSIs). The deposition characteristics of tantalum oxy-nitride (TaON) films have been investigated by using an electron cyclotron resonance (ECR) plasma sputtering without external substrate heating. A pure tantalum metal target was used as raw material supply combined with gases of oxygen and nitrogen. The electrical characteristics of the deposited films were examined by using MIM capacitor of ruthenium blanket electrodes and aluminum top pad electrodes. The electrical characteristics of the deposited films were changed from metallic conductive states to high-k dielectric states by the mixture ratio of oxygen and nitrogen. For the dielectric films, in high concentrations of oxygen gas, the deposited tantalum oxide (Ta@sub 2@O@sub 5@) films have a refractive index of 2.15 at 632.8 nm wavelength, high dielectric constant of 25, and high breakdown-strength of 5MV/cm. By controlling the oxygen gas concentrations in moderate low region, films of TaON have been stably obtained with the refractive indices of around 2.9 at 632.8 nm wavelength, higher dielectric constants of over 35 and breakdown-strengths of around 1MV/cm. In spite of low substrate temperature without external heating, high quality TaON films have successively obtained. The TaON films deposited by the ECR plasma sputtering can be applicable to the capacitor dielectrics and gate oxides for Si-LSIs, compound MIS-FETs, and the drive circuit devices for LCDs.

9:20am **PS2+TF-WeM5 In Situ Studies of Reaction Mechanisms during Plasma-Assisted Atomic Layer Deposition of Al@sub 2@O@sub 3@**, ***S.B.S. Heil***[1]*, P. Kudlacek, E. Langereis, R. Engeln, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Extending the atomic layer deposition (ALD) technique with plasma processes (i.e., plasma-assisted ALD or PA-ALD) opens up new routes that are difficult to attain by pure thermal ALD. In particular the ability to deposit high-quality oxide films at low substrate temperatures using an O@sub2@ plasma has recently expanded the interest in ALD from solely semiconductor manufacturing to upcoming fields such as photovoltaics and flexible electronics. However, for PA-ALD the reaction mechanisms leading to film formation have not been extensively studied and especially for the reactions occurring during the plasma step several questions still remain unanswered. In this contribution, we present an in situ study of the PA-ALD process of Al@sub2@O@sub3@ from Al(CH@sub3@)@sub3@ (trimethylaluminum, TMA) and O@sub2@ plasma. Employing a combination of quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), and optical emission spectroscopy (OES) an insight into the plasma species, reaction products, and surface chemistry is gained. For example, QMS showed that during the plasma step H@sub2@O and CO@sub2@ are formed from the surface CH@sub3@ groups in a combustion like reaction. This is supported by time-resolved OES in which the consumption of oxygen species and the emission by excited CO molecules were detected until the process reached saturation (<0.5 s). From QCM and QMS measurements it was determined that during the precursor step the TMA reacts mainly bifunctionally with the surface OH groups splitting of ~1.8 CH@sub3@ ligands as CH@sub4@. QCM measurements were correlated with in situ spectroscopic ellipsometry giving more detailed information about film growth during PA-ALD of Al@sub2@O@sub3@. The combustion like reaction occurring in the deposition of Al@sub2@O@sub3@ is expected to be generic for plasma-assisted ALD processes of oxides from metalorganic precursors.

9:40am **PS2+TF-WeM6 XPS Study of Plasma Pretreatment of PEN and Related Polymer Substrates to Enhance Atomic Layer Deposition of Aluminum Oxide**, ***E.S. Brandt,*** *J.M. Grace,* Eastman Kodak Company

The role of water plasma pretreatment of polymer substrates to promote atomic layer deposition (ALD) of aluminum oxide from dimethylaluminum isopropoxide (DMAI) is investigated using an in situ ALD deposition chamber that is interfaced directly to the UHV system of an X-ray photoelectron spectrometer. Using X-ray photoelectron spectroscopy (XPS), it is shown that treatment by water plasma incorporates surface hydroxyl functional groups, which enhance the deposition of aluminum oxide by approximately an order of magnitude on poly(ethylene naphthalate) (PEN), and activates an otherwise inert polystyrene (PS) surface to alumina deposition when DMAI and water are used as ALD reactants. By contrast, under our reaction conditions, the intrinsic reactivity of the highly hydroxylated surface of polyvinyl alcohol (PVA) toward repeated DMAI/water ALD cycles is not significantly enhanced by water plasma pretreatment. The data suggest that in the absence of inherently reactive surface functional groups (e.g., hydroxyl groups) to promote chemisorption of the metal-bearing precursor, some polymers, including PS and PEN, require surface functionalization (e.g., water plasma treatment) to initiate ALD growth of metal oxides.

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

10:40am **PS2+TF-WeM9 The Use of Pulse-Shaped Substrate Bias for Energy-Selective Ion Bombardment During Amorphous Si Deposition***, **I.T. Martin**, M.A. Blauw, R. Engeln,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

The role of neutrals during expanding thermal plasma (ETP) deposition of a-Si:H has been thoroughly studied in the literature. Less attention has been paid to ions, both because ion flux is low compared to neutral flux, and the remote nature of the plasma source results in low ion energies, <2eV. Ion bombardment effects depend on ion energy as different thresholds exist for enhancing vs. damaging processes. RF-biasing has previously been used to increase ion energy; appropriate substrate voltages resulted in an increase in the photoconductivity of a-Si:H. A disadvantage of rf-biasing is that the resulting ion energy distributions (IEDs) are broad and bimodal. We have applied the pulse-shaped substrate bias technique developed by Wendt and coworkers@footnote 1@ to ETP a-Si:H deposition, which results in narrow IEDs. This improves ion energy control, allowing further optimization of materials properties. Preliminary data demonstrate that the effect of this bias varies for different plasma conditions; materials deposited in plasmas with low ion currents (<3mA) and high deposition rates (~5nm/s) are unaffected by the bias. The setup also allows us to determine ion flux to the substrate. Data show that increasing H@sub 2@ flow results in decreased ion flux, consistent with earlier Langmuir probe measurements. Interestingly, ion flux increases with increasing substrate potential, suggesting the formation of additional plasma in front of the substrate. Materials were deposited with varying Ar:H@sub 2@:SiH@sub 4@ flows, and a range of substrate biases (0 to -140V). Films were characterized using FTIR and photoconductivity measurements; differences in deposition rate, refractive index, hydrogen content and photoconductivity as a function of substrate bias will be discussed. Results are compared to a-Si:H deposited using rf-biasing, and to other materials deposited using a pulse-shaped bias. @FootnoteText@ @footnote 1@S.B. Wang and A.E. Wendt, J. Appl. Phys. 88, 643 (2000).

11:00am **PS2+TF-WeM10 Effects of Clusters and Higher-Order Silane Related Radicals on Stability of a-Si:H Films Deposited by Plasma CVD***, **K. Koga**, H. Miyahara, G. Yuan, A. Genot, S. Iwashita, W.M. Nakamura, M. Shiratani,* Kyushu University, Japan

Light-induced degradation of hydrogenated amorphous silicon (a-Si:H) is one of the most important issues for a-Si:H solar cells.@footnote 1@ Recently, we have succeeded in depositing highly stable a-Si:H films by using a multi-hollow discharge plasma CVD method.@footnote 2@ We can obtain information about species responsible for degrading stability, because stable a-Si:H films are deposited in the upstream region from the discharges while metastable ones are in the downstream region in the multi-hollow discharge plasma CVD reactor. To identify such species, we detected clusters and higher order silane related radicals both in the upstream and downstream region. The amount of amorphous clusters in the upstream region is by more than two orders of magnitude lower than that in the downstream, whereas densities of Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ in the upstream related radicals is 0.3 - 0.7 times as low as those in the downstream even for a high gas velocity of 52 cm/s. Therefore, the multi-hollow discharge plasma CVD method together with a high gas velocity is effective in suppressing volume fraction of clusters incorporated into the films deposited in the upstream region, while such combination has little effects on those of Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ related radicals. These results suggest that amorphous clusters formed in the discharges are one of the species responsible for degrading stability of films, whereas Si@sub 2@H@sub 6@ and Si@sub 3@H@sub 8@ related radicals are not. @FootnoteText@ @footnote 1@R. E. I. Schropp and M. Zeman, "Amorphous and Microcrystalline Silicon Solar Cells", Kluwer Academic Publishers, Boston, 1998, p. 99.@footnote 2@K. Koga, et al., Jpn . J. Appl. Phys., 48 (2005) L1430.

11:20am **PS2+TF-WeM11 Methods of Producing Plasma Enhanced CVD Silicon Nitride Thin Films with High Compressive and Tensile Stress***, **M.P. Belyansky**, N. Klymko, A. Madan, M. Chace, S. Molis, P.A. Ronsheim, J. Kempisty, A. Mallikarjunan, Y. Li,* IBM Microelectronics

High stress plasma enhanced chemical vapor deposition (PECVD) films are becoming an integral part of the state-of the-art metal oxide semiconductor field effect transistor (MOSFET) technology. Generation of a uniaxial strain in a silicon channel is shown to substantially increase device speed, which is achieved by an application of high stress tensile or compressive silicon nitride (SiN) films leading to either electron or hole mobility enhancement respectively. Various methods of generating high stress in thin PECVD SiN films are discussed. Besides the mainstream variation of plasma power and other process parameters, novel techniques of stress build-up in thin films like creation of specific types of interfaces and multilayer structures by PECVD or exposure of SiN films to ultraviolet (UV) radiation are reported. Thin PECVD SiN films (about 50nm) have been analyzed by a variety of analytical techniques including Fourier Transform Infrared Spectroscopy (FTIR), X-ray reflectivity (XRR), Secondary Ion Mass Spectrometry (SIMS) and Rutherford backscattering (RBS) to collect data on bonding, density and chemical composition. Mechanisms of stress formation in both compressive and tensile SiN thin films are discussed. Level of bonded hydrogen as well as film density has been found to correlate with film stress. Interface formation and creation of a multilayer structure helps to build up more stress compared to a standard single layer film deposition. Both the density and number of interfaces in a film, characterized by XRR, affect the stress. Exposure of multilayer SiN films to elevated temperature results in a loss of a well-defined interface structure and leads to the predictable increase in tension and degradation in compressive stress. Interface composition and barrier properties of multilayer films are discussed. Effect of UV radiation exposure on PECVD SiN and the resulting increase in film tensile stress is also delineated.

11:40am **PS2+TF-WeM12 Analyses of CH4/H2 RF Plasma and Iron Catalysts for Control of Carbon Nanotube Growth***, A. Okita, **Y. Suda**, A. Ozeki,* Hokkaido University, Japan*; A. Oda,* Nagoya Institute of Technology, Japan*; J. Nakamura,* Tsukuba University, Japan*; K. Bhattacharyya, H. Sugawara, Y. Sakai,* Hokkaido University, Japan

We have studied CH@sub 4@/H@sub 2@ gas mixture RF plasma by one-dimensional fluid modeling and iron catalysts by X-ray photoelectron spectroscopy (XPS) for controlling carbon nanotube (CNT) growth in plasma-enhanced CVD (PECVD).@footnote 1,2@ To control CNT growth in terms of length, diameter, number density and orientation, understanding the behavior of hydrocarbon (C@sub x@H@sub y@) radicals and ions onto metal-catalyzed substrate becomes important. So far, we have shown that the carbon amount evaluated from the fluxes of C@sub x@H@sub y@ radicals and ions by the modeling is reasonably consistent with that in CNTs grown by PECVD.@footnote 1@ The PECVD setup sustains the CH@sub 4@/H@sub 2@ or H@sub 2@ plasma in a pressure range of 1-10 Torr. The substrate temperature is kept at 550°C for reduction and 650°C for growth. Length, diameter and number density of the CNTs grown are analyzed. The carbon atom density in a graphene sheet (3.81X10@super 15@ atoms/cm@super 2@) is used to evaluate the amount of carbon in CNTs. One-dimensional fluid modeling analyzes the densities and fluxes of C@sub x@H@sub y@ radicals and ions between powered and grounded electrodes. Assuming the sticking probability of C@sub x@H@sub y@ radicals on substrate: CH, 0.025; CH@sub 2@, 0.025; CH@sub 3@, 0.01; C@sub 2@H@sub 5@, 0.01; H, 0.01,@footnote 3@, we predict the amount of carbon which are supplied from the plasma and incorporated into CNTs. Very recently, we have shown that the content of iron oxide in the catalyst analyzed by XPS correlates with CNT growth.@footnote 2@ In this presentation, we discuss the growth speed of CNTs by both the PECVD and modeling and the CNT growth duration by XPS analysis. @FootnoteText@@footnote 1@A. Okita, et al., J. Appl. Phys., 99 (2006) 014302 @footnote 2@A. Okita, et al, Jpn. J. Appl. Phys. (accepted) @footnote 3@I. B. Denysenko, et al., J. Appl. Phys. 95, 2713 (2004).

12:00pm **PS2+TF-WeM13 Increase of O(@super 1@D) Metastables by Rare-Gas Diluted O@sub 2@ Plasma and Application to the Oxide Growth***, **T. Kitajima**,* National Defense Academy of Japan, Japan*; T. Nakano,* National Defense Academy of Japan*; T. Makabe,* Keio University, Japan

Rare gas diluted O@sub 2@ plasmas are gaining interests for application to high quality SiO@sub 2@ film formation. Especially, metastable O(@super 1@D) atoms produced in rare gas diluted O@sub 2@ plasma is believed to promote higher production rate of the oxide films. We have found the increase of O(@super 1@D) atoms in rare gas diluted O@sub 2@ RF plasma measured by VUV absorption spectroscopy.@footnote 1@ The increase of the O(@super 1@D) density is due to the increase of rare gas metastables that selectively produce O(@super 1@D) atoms via dissociative excitation of O@sub 2@. Among rare gas species, Krypton dilution enables highest O(@super 1@D) density. Then we applied the increased O(@super 1@D) flux of the Kr diluted O@sub 2@ plasma to the formation of SiO@sub 2@ films. Silicon substrate is flashed in the vacuum by direct current heating to form bare Si(001) surface. The surface is exposed to the Inductive coupled plasma operated at 70 MHz in O@sub 2@(3%)/Kr at 0.1 Torr for oxidation. After the oxidation, the sample is

introduced to the UHV chamber which have a contact mode AFM for film evaluation. The topography and breakdown voltage of the SiO@sub 2@ films are measured by the biased AFM tip. The topographic images and breakdown current map shows the uniform oxide formation of the rare-gas diluted O@sub 2@ plasma. The breakdown voltage of the film is nearly same to the one of pure O@sub 2@ plasma case. Regarding the increase and the decrease of the O(@super 1@D) and the ground state O(@super 3@P) flux to the surface during oxidation, O(@super 1@D) atom has an order higher oxidation rate of Si(001) than O(@super 3@P). The results show the enhancement of oxidation rate of silicon with using increased O(@super 1@D) selectively produced in rare-gas diluted O@sub 2@ plasma. @FootnoteText@ @footnote 1@ T.Kitajima, T.Nakano, and T.Makabe, Appl. Phys. Lett. 88, 091501 (2006).

Plasma Science and Technology
Room 2009 - Session PS1-WeA

Plasma-Wall Interactions and Plasma Sources

Moderator: J.P. Booth, Lam Research Corporation

2:00pm **PS1-WeA1 Plasma-Wall Interactions in an Inductively Coupled Plasma Etching Reactor***, **S. Ullal**,* Lam Research Corporation **INVITED**

Wafer-to-wafer process reproducibility is one of the major concerns in plasma etching of thin films with high density inductively coupled reactors, which are widely used for integrated circuit manufacturing. These reactors are typically operated at low pressures, where the mean free path of species in the plasma is on the order of the reactor dimensions, and reactive radicals collide as often with the chamber walls as they do with each other in the gas phase. Thus, the plasma chamber walls play a crucial role in determining the discharge properties such as ion density, electron temperature, and species concentration. Often, a stack of thin films of different materials is etched sequentially using multiple gases in the same chamber. Chemicals used and/or produced during the etching of one film may adsorb or deposit on the walls of the reactor and alter the chemical reactivity of the walls. The changing wall conditions cause variations in the discharge properties directly affecting etching reproducibility. This problem of process sensitivity to the wall conditions has been known for a long time but its management has remained an art. This talk will review the advances made towards improving the understanding of plasma-wall interactions using various plasma diagnostic techniques as applied to specific chemistries used for plasma etching proceses used in integrated circuit manufacturing.

2:40pm **PS1-WeA3 Impact of Chamber Walls on Radical Densities in Cl@sub 2@ ICP Plasmas***, **G. Cunge**,* CNRS-LTM, France*; N. Sadeghi,* CNRS, France*; R. Ramos,* Freescale Semiconductor Inc., France*; O. Joubert,* CNRS-LTM, France

The radical densities in low pressure high-density discharges are controlled mainly by chemical reactions occurring at the reactor walls. This sensitivity of halogen-based plasmas to the chamber walls conditions is known for long time and is at the origin of process drifts. By using laser absorption at 355 nm we have measured the absolute density of Cl@sub 2@ molecules in a typical Cl@sub 2@ plasma operating either in a clean reactor or in a reactor coated with a SiOCl, CCl@sub x@ or TiOCl@sub x@ layer. We report that under identical plasma operating conditions, the Cl@sub 2@ mole fraction in the plasma can vary from 0.1 to 0.6 depending on the chemical nature of the chamber wall coatings. We have then measured the time variation of Cl@sub 2@ and SiCl@sub x@ (x=0-2;4) etch products densities (by UV absorption and mass spectrometry (MS)) during silicon etching both in clean and SiOCl-coated reactor. From the Cl mass balance in the system and from MS measurements we concluded that several species are produced from the SiOCl-coated reactor walls, including heavy Si@sub x@O@sub y@Cl@sub z@ species (with x up to 4). Furthermore, it is obvious from these measurements that the quartz surface below the RF coil behaves differently than the other reactor walls surfaces, and plays an important role in controlling the plasma chemistry. As a matter of fact, due to electrostatic coupling, this part of the equipment is bombarded by more energetic ions than the floating walls of the chamber and is thus an efficient region of production (/loss) of reactive species. Furthermore, the sudden formation or disappearance of a thin conductive layer below the RF coil can lead to plasma instabilities by influencing the electromagnetic coupling between the RF coil and the plasma. The impact of these phenomenons on metal gate etching processes will be discussed in details.

3:00pm **PS1-WeA4 Influence of Bombarding Energy on Stabilization of Radical Density of Fluorocarbon Plasma***, **K. Kumagai**,* Chubu University, Japan*; T. Tatsumi, K. Oshima, K. Nagahata,* Sony Corporation, Japan*; K. Nakamura,* Chubu University, Japan

Fluorocarbon discharges have been widely used for etching processes of dielectric thin films for microfabrication. However, these have suffered from various problems, in particular, repeatability of the etching characteristics. The problem becomes recently severe due to narrow process margin for next generation ULSI devices. One of the major origins is plasma-surface interaction on polymer-deposited vessel wall, leading to significant time-variation of radical composition of the plasma. Alternating ion bombardment (AIB) method has been proposed to reduce such interactions by applying an RF bias to the chamber wall. We reports on suppression of the temporal density variation of fluorocarbon radicals caused by removal of the deposited polymer with ion bombardment as well as effects of ion bombarding energy on the density variation. 13.56 MHz inductively-coupled plasmas were produced in Ar-diluted C@sub 4@F@sub 8@ gases in a stainless steel chamber in which two semi-cylindrical electrodes were set. Oxygen plasma pretreatments were performed before each the discharge. A 400 kHz RF source served alternating negative bias to the electrodes, and the AIB could control the deposition rate of the polymer on the biased wall. When the polymer deposition was suppressed with the AIB, the radical density reached a steady state more quickly after the discharge initiation. However the rise time of the radical density was seriously influenced by the ion bombarding energy. Significant polymer deposition occurred at the wall at a too low ion bombarding energy. On the other hand, when the ion bombarding energy is too high for suppression of the polymer deposition, thickness of fluorocarbon reaction layer formed on the wall surface increased, resulting in longer time to be required to reach steady state surface conditions. Thus, there was an optimal ion bombarding energy for fast stabilization of the surface condition and the radical density.

3:20pm **PS1-WeA5 Modeling of Seasoning of Reactors: Effects of Ion Energy Distributions to Chamber Walls****, A. Agarwal,* University of Illinois at Urbana-Champaign*; **M.J. Kushner**,* Iowa State University

Wafer to wafer process reproducibility during plasma etching often depends on the conditioning of the walls of the reactor. Deposition of passivation on chamber walls can change the reactive sticking coefficients for radicals, thereby changing the composition of the radical and ion flux to the substrate. Ion bombardment of the walls may affect the passivation coverage or production of etch influencing species through activation of sites or sputtering. As such the spatial distribution of ion energies on the walls and their evolution as the chamber seasons are important. These seasoning processes may occur during a single etching sequence or recipe due to there being incomplete initial seasoning or there being a change in radical fluxes to the walls. In this talk, the seasoning of plasma etching reactors will be discussed using results from a computational investigation. The Surface Chemistry Module and Sputter Module of the Hybrid Plasma Equipment Model were modified to obtain the ion energy distributions to all surfaces inside the reactor and to use them to calculate energy dependent surface reaction rates. Sputtered, energetic products from passivated side walls, and their transport to the wafer, were also accounted for using the same methodology as in magnetron sputtering. Results will be discussed for the seasoning of ICP reactors using Ar/Cl@sub 2@ gas mixtures; and CCP reactors using Ar/C@sub 4@F@sub 8@ mixtures. The consequences on reactive fluxes (magnitude and energy) to the substrate due to both wall sputtering and changes in reactive sticking coefficients will be presented. @FootnoteText@ *Work supported by Semiconductor Research Corp. and the National Science Foundation.

3:40pm **PS1-WeA6 Plasma Requirements from Dielectric Etch Systems for Advanced Materials***, **D.J. Hoffman**,* Applied Materials **INVITED**

As materials of dielectric etch migrate to meet the needs of the 32 nm node, the needs in ion energy, density, ion energy distribution, and electron energy are expected to shift and mandate modifications to tool design. Specifically, low-k dielectric with k-value below 2.5 created need dramatically different energy spectrum than a deep etch into a very hard material. Other functions, such as chamber cleaning, ultra soft etch, via etch, and trench necessitate using densities that range from low 10@super 10@ cm@super -3@ to high 10@super 10@ cm@super -3@, ion energies in the range of 50 V to thousands of volts, and energy spread of 20 to 80 %. In this paper we, examine how 3-frequency capacitive systems can produce the requisite plasma parameters. In each capacitive system, the ability to create density is controlled by a) characteristic impedance, which then determines the voltage at relevant power b) given the voltage of the system and the plasma intrinsic rectification- the division between sheath creation and density creation, and c) given ion energy transit times for a characteristic density and sheath voltage, ion energy spread. With the process need establishing plasma targets, we compare how various frequency ranges can be used to produce the desired plasma.

4:20pm **PS1-WeA8 Frequency Dependent Ion Kinetics in a 300 mm Dual-Frequency Capacitively Coupled Plasma Reactor***, **G.A. Hebner**, E.V. Barnat, P.A. Miller,* Sandia National Laboratories*; A.M. Paterson, J.P. Holland,* Applied Materials

Argon ion kinetics were measured in a dual frequency, capacitively coupled 300 mm chamber. Laser induced fluorescence measurements of the argon ion metastable lineshape yield information on the ion temperature, density and drift velocity. The spatially-resolved LIF technique is a nonperturbative

probe to investigate energy deposition mechanisms, ion energy distribution functions, charge exchange reactions, neutral heating, and plasma potential gradients within the plasma. This talk will discuss ion characteristics for a single rf frequency drive (13, 60 and 160 MHz), combinations of rf drive frequencies, as well as scaling with pressure (10 to 70 mTorr) , rf power, and radial position. We find that the ion density increased linearly with rf power, as did the electron density, indicating the ion metastable state is formed from direct impact ionization. The ion temperature was on the order of 500 K. This is consistent with other measurements in capacitively coupled systems at 13 MHz but considerably less than values in inductively coupled systems (1000 to 9000 K). The lower ion temperature may reduce molecular decomposition. Radially resolved ion drift velocity measurements show the radial drift velocity can be lower at 60 MHZ than 13 MHz. Additional details 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 Energys National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:40pm **PS1-WeA9 Spatial and Temporal Structure of a Sheath formed in a 300 mm, Dual-Frequency Capacitive Argon Discharge***, **E.V. Barnat**, G.A. Hebner, P.A. Miller,* Sandia National Laboratories*; A.M. Paterson, J.P. Holland,* Applied Materials

The spatial and temporal distributions of the electric fields of a sheath formed by a dual-frequency driven capacitive argon discharge are measured as functions of relative mixing between a low frequency current (13.56 MHz) and high frequency current (67.8 MHz). This is the first time a Stark effect based technique has been employed to measure sheaths of this nature. We find that for a given total input power, as the high frequency power increases, both the total voltage across the sheath and the thickness of the sheath decreases. We also find that the temporal evolution of the potential across the sheath as well as the sheath thickness contain both rf components and that the high frequency oscillations become more prominent with increased high frequency power. For insight, comparisons of the measured spatial and temporal profiles are made to computational models commonly employed in the literature. These models include the collisional rf sheath model of Lieberman@footnote 1@ and extended to dual frequencies by Robiche@footnote 2@ et al. Where possible, we compare on our measured trends to those predicted by the models, which in general, show good agreement. Included in the discussion are the effects the edge has on the distribution of the electric fields and the effects the driving frequency has on the field distribution across the wafer. @FootnoteText@ @footnote 1@ M.A.Liberman, IEEE Trans. Plasma Sci. 17, 338 (1989).@footnote 2@ J. Robiche, P. C. Boyle, M. M. Turner and A. R. Ellingboe, J. Phys. D: Appl. Phys 36, 1810 (2003).

Plasma Science and Technology
Room 2011 - Session PS2-WeA

Atmospheric and Microplasmas

Moderator: D.J. Economou, University of Houston

2:00pm **PS2-WeA1 Use of Hydrogen or Oxygen Atmospheric Pressure Plasmas for the Surface Treatment of Metals***, E. Michel,* Unviersité Libre de Bruxelles, Belgium*; E. Silberberg,* ARL, Arcelor Group*; **F. Reniers**,* Unviersité Libre de Bruxelles, Belgium

Oxygen or hydrogen-based dielectric barrier discharges were used to remove organic contaminants from steel surfaces or to reduce surface oxides on various metals (copper, iron). Contaminated steel surfaces were treated using atmospheric pressure oxygen based plasmas 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@sub2@, at atmospheric pressure, or pure oxygen at a reduced 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 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 gas composition on the kinetics of decontamination was studied. The resulting surface state of steel was investigated using AES and X-ray photoelectron spectroscopy. A macroscopic model for the kinetics of decontamination is proposed. Oxidised steel and copper surfaces were then exposed to low pressure hydrogen plasmas and high pressure hydrogen-helium plasmas. Although the DBD configuration was similar to the one developed for oxygen plasmas, the plasma reactor was attached to a XPS-UHV chamber to avoid post oxidation during transfer in air. Complete reduction of iron oxide and copper oxide could be achieved. The relationships between the plasma parameter (pressure, charge density, and frequency), the OES intensity of the hydrogen line, and the efficiency of surface oxide reduction were established for iron oxide.

2:20pm **PS2-WeA2 Fluoropolymer Deposition and Polymer Fluorination by Atmospheric Pressure Glow Dielectric Barrier Discharges***, **F. Fanelli**, F. Fracassi, R. d'Agostino,* University of Bari, Italy

In this contribution we report our latest results on the PECVD of fluorocarbon thin films from glow dielectric barrier discharges (GDBDs) fed with He-C@sub 3@F@sub 6@ and He-C@sub 3@F@sub 8@-H@sub 2@ gas mixtures as well as on the fluorination of polymeric substrates by He-CF@sub 4@ GDBDs. The atmospheric plasma was generated in a parallel plate electrode configuration (5 mm gap) by applying an AC high voltage (< 4 kV@sub p-p@) in the frequency range 15 - 30 kHz. The effect of several process parameters (i.e. feed composition, frequency, voltage, etc.) was investigated inside the GDBD existence domain adequately evaluated by electrical measurements. Surface composition and structure were investigated through FTIR, X-ray Photoelectron Spectroscopy, Water Contact Angle measurements (WCA) and Scanning Electron Microscopy. He-C@sub 3@F@sub 6@ fed GDBDs allowed to deposit fluorocarbon films with F/C ratio of 1.5 at a deposition rate up to 35 nm/min. The investigation of He-C@sub 3@F@sub 8@-H@sub 2@ fed GDBDs showed that it is possible to tune the F/C ratio from 1.5 to 0.7 and to change the cross-linking degree of the coatings by varying the hydrogen concentration in the feed. H@sub 2@ admission promotes the increase of the deposition rate that is maximum when the fluorocarbon-to-hydrogen ratio is close to 1. Preliminary results from fluorination of polypropylene (PP) and polyethyleneterephtalate (PET) substrates with He-CF@sub 4@ mixtures allowed to observe the grafting of fluorinated functionalities which increased the WCA values up to 115° and 109° for PP and PET, respectively. Results of optical emission spectroscopy investigation of the plasma phase will be also presented.

2:40pm **PS2-WeA3 Numerical and Experimental Study of Microhollow Cathode Sustained Discharges in Ar and O2 at Relative High Pressure***, **E. Muñoz-Serrano**, T. Callegari, G. Hagelaar, L. Pitchford, J.P. Boeuf,* CPAT - CNRS, France **INVITED**

Many research groups around the world are now actively investigating ways of generating and maintaining a stable, non-thermal, high-pressure plasma in electric discharges. Since the initial work of Schoenbach and his colleagues, it is now well established that such plasmas can be generated and maintained in discharges in small - 100's of micron-sized - geometries. The simplest such system consists of a cathode/dielectric/anode sandwich through which a cylindrical hole of some 200 microns is drilled. This is refered to as a MicroHollow Cathode Discharges or MHCD. Our work is focused on the study of the parameters that characterize the behaviour of a Micro Cathode Sustained (MCS) discharge@Footnote 1@ in which a third planar electrode (anode A2) is placed parallel at some distance (1 cm) from the anode (A1) of the MHCD sandwich. Thus, the MHCD is used as an electron source to form a higher plasma volume between the MHCD and the anode A2. Our experimental results to date suggest that the plasma in the MCS region can be treated like a positive column where the plasma is sustained by a local balance of charged particle losses and production processes. Our 2D model of the radially expanding positive column plasma in the MCS region is qualitatively consistent with experimental results in argon and in oxygen discharges. Results from these experimental and numerical results will be presented to illustrate the plasma properties that can be achieved in microdischarges in this MCS configuration. We would like to acknowledge the contribution of collaborative the experiments of V Puech (LPGP, Orsay) and A Rousseau (LPTP, Palaiseau) conducted in microcell geometries.@FootnoteText@@footnote 1@R.H. Stark and K.H. Schoenbach, J. Appl. Phys. 85 (1999) 2075.

3:20pm **PS2-WeA5 Spatially Resolved Gas Temperature Measurements in an Atmospheric Pressure DC Glow Microdischarge with Raman Scattering***, **S.G. Belostotskiy**[1], Q. Wang, V.M. Donnelly, D.J. Economou,* University of Houston*; N. Sadeghi,* Universite J. Fourier de Grenoble, France

Spatially resolved rotational Raman spectroscopy of ground state nitrogen N@sub 2@(X@super 1@@SIGMA@@sub g@@super +@) was used to

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

measure the gas temperature (T@sub g@) in a nitrogen dc glow microdischarge (gap between electrodes d ~ 500 µm). An original backscattering, confocal optical system was developed for collecting Raman spectra. Stray laser light and Raleigh scattering were blocked by using a triple grating monochromator and spatial filters, designed specifically for these experiments. The optical system provided a spatial resolution of <100 µm. Gas temperatures were determined by matching experimental spectra to model spectra obtained by convolution of theoretical line intensities with the apparatus spectral resolution, with Tg as the adjustable parameter. T@sub g@ was determined as a function of pressure and discharge current density (P = 400 - 760 Torr, j@sub d@ = 200 - 1000 mA/cm@super 2@). Midway between the electrodes, T@sub g@ increased linearly with j@sub d@, reaching 420 K at 1000 mA/cm@super 2@ j@sub d@ for a pressure of 720 Torr. Spatially resolved gas temperature measurements will also be presented and discussed in combination with a mathematical model for gas heating in the microplasma.

3:40pm **PS2-WeA6 Experimental and Theoretical Studies of Atmospheric Pressure Direct Current Microplasma Argon Discharges***, **Q. Wang**,* University of Houston*; I. Koleva,* Sofia University, Bulgaria*; D.J. Economou, V.M. Donnelly,* University of Houston*; N. Sadeghi,* University Joseph Fourier-Grenoble & CNRS, France

A combination of plasma diagnostics and modeling were performed on a slot-type DC microplasma discharge in argon at atmospheric pressures. The gas temperature was measured by N@sub 2@ emission spectroscopy (C -> B transition) by adding small quantities of nitrogen (B rotational spectra, and the gas temperature was determined from the lower of the two temperature values. At 760 Torr and 18 kW/cm@super 3@ power density, the gas temperature was between 500 K and 1100 K, depending on position between the electrodes. Electron densities were determined from the spectral line broadening of H-@beta@ emission. The electron density in the bulk plasma was the 10@super 14@ cm@super -3@ range. A model of a DC argon microplasma discharge was in agreement with experimental data. Spatially resolved gas temperature measurements as a function of gas flow through the microplasma also agreed with the model. The gas temperature decreased with increasing gas flow due to convective removal of heat. The gas temperature peaked off axis near the cathode as ions accelerated in the cathode sheath and deposited part of their energy in frequent collisions with the neutral gas.

4:00pm **PS2-WeA7 Use of Dual Atmospheric Microdischarges for Manipulating the Growth of Silicon Nanoparticles***, **N.A. Brunelli**, K.P. Gipias, R.C. Flagan,* California Institute of Technology

Atmospheric microdicharges have been shown@footnote 1@ to produce Silicon nanoparticles between 1-2 nm in diameter, which exhibit intense photoluminescence emission at 420 nm with a quantum efficiency of 30%. It is desirable to obtain emission at longer wavelengths for imaging applcations, by increasing the diameter of the nanoparticles. However, it has been exceedingly difficult to manipulate the nanoparticle size in a single microdischarge, where perturbations to the growth conditions seem to only influence the number of particles produced while the size remains invariant. We demonstrate here that by using two microdischarges in series that silicon nanoparticles generated in the first microdischarge can be overgrown to larger sizes in the second microdischarge. The addition of precursor in the second microdischarge and adjustment of other operating parameters allows the particle size to be tuned. We quantify this claim by using a new ultrafine radial differential mobility analyzer (UF-rDMA) immediately after the second microdischarge to monitor in real time the particle size. The particles are then deposited on solid substrates for independent size verification by atomic force microscopy (AFM). Finally, we characterize the nanoparticles by photoluminescence and transmission electron microscopy. @FootnoteText@ @footnote 1@ R.M. Sankaran, et al. Nano Lett. 5 (3) 2005.

4:20pm **PS2-WeA8 Development of Multi-Micro Hollow Cathode Lamp with Metallic-Element-Emission Allay***, **T. Ohta**, S. Taneda, M. Ito,* Wakayama University, Japan*; S. Takashima,* Nagoya University, Japan*; H. Kano,* NU EcoEngineering CO., LTD., Japan*; S. Den,* Katagiri Engineering CO., LTD., Japan*; M. Hori,* Nagoya University, Japan

For quantitative analysis of metallic elements, the atomic absorption spectrometry has been widely used. The development of the compact light source, which emits simultaneous multi-atomic lines for the analysis, is required, since the analysis should be performed quickly on-site in the environmental field. Therefore, we developed the multi-light source using micro hollow cathode discharge. Micro hollow cathode discharge can be stably generated in high-pressure without an arc discharge, which destroys the devices. The four Cu pipes attached with metallic wires, which are Fe, Mo, and Brass respectively, were used as a cathode. The inside diameter of Cu pipe was 0.7 mm. The Cu mesh as an anode was set at the distance of 160?m from the cathode. The discharge was generated by using helium as a working gas at the pressure of 0.02 MPa, the current of 71 mA, and the discharge voltage of 320 V. The emissions of four metallic elements from the each pipe were simultaneously obtained. The analysis line of Cu (324.74 nm), Zn (213.86 nm), and Fe (344.06 nm), and resonance line of Mo (379.83 nm) were observed. The emission intensities of metallic elements increase with a decrease in the pressure. The pD, where p is a pressure and D is a cathode hole diameter, was 1.1 Torr cm and the discharge was stably generated with hollow cathode effect. The multi-light source using micro hollow cathode discharge was successfully developed. The multi-micro hollow cathode discharge would open the window to analyze the various metallic elements simultaneously by changing the wire elements.

4:40pm **PS2-WeA9 Finite Element Analysis of Atmospheric Pressure RF-excited Plasma Needle***, **Y. Sakiyama**,* University of Tokyo, Japan*; D.B. Graves,* University of California, Berkeley

The atmospheric pressure RF-excited plasma needle is a non-thermal discharge powered at 13.56 MHz with a localized plasma sustained at the sharp tip of a thin cylindrical conducting electrode. Using a finite element solution to the governing fluid equations, we identify two discharge modes of the plasma needle as well as the transition mechanism. The gas used is helium with 0.1% nitrogen addition. The needle has a point-to-plane geometry with a radius of 3 µm at the tip, 150 µm at the base and an inter-electrode gap of 1 mm. The plasma needle operates as a corona discharge at low power and a glow discharge above a critical power. The discharge power increases but the discharge voltage drops abruptly by a factor of about 2 in the corona-glow transition. In corona-mode, the peak plasma density and ionization is confined near the needle tip. Penning ionization of the trace nitrogen gas is the dominant ionization reaction and displacement current dominates over the conduction current. On the other hand, the plasma spreads back along the needle surface in glow-mode. Direct ionization of helium prevails over Penning ionization and conduction current accounts for 80% of the total current in glow mode. The corona-glow transition is also characterized by a dramatic decrease in sheath thickness and an order of magnitude increase in plasma density and volume-averaged ionization. The transition is observed whether or not secondary electron emission is included in the model. The influence of species such as oxygen and water vapor, and the role of forced convection towards a surface to be treated, will be also presented. Experimental validation of the model predictions is discussed.

Plasma Science and Technology
Room 2009 - Session PS1+BI-ThM

Plasmas in Bioscience

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

8:00am **PS1+BI-ThM1 Study of Plasma Modified PTFE for Biological Applications : Relationship between Non Fouling Properties - Plasma Treatment - Surface Composition and Surface Roughness***, **N. Vandencasteele** [1] ,* Université Libre de Bruxelles, Belgium*; B. Nisol,* Unviersité Libre de Bruxelles, Belgium*; P. Viville, R. Lazzaroni,* Université de Mons-Hainaut, Belgium*; D.G. Castner,* University of Washington*; F. Reniers,* Unviersité Libre de Bruxelles, Belgium

Polytetrafluoroethylene was treated by oxygen or nitrogen RF low pressure plasmas. The modified samples were characterized by XPS for surface composition, contact angle for surface energy and atomic force microscopy for surface roughness. The adsorption of bovine serum albumine (BSA) was used as a probe for the (non)fouling properties and potential biological applications. Evidence for BSA adsorption was determined by the appearance or the increase of the N 1s XPS peak. PTFE modified by Nitrogen plasma shows a strong decrease of the contact angle that has previously been correlated to an increase of the nitrogen surface concentration due to grafting and to a decrease of the fluorine concentration.@footnote 1@ Further exposure to BSA leads to an increase of the N 1s signal, and to a concomitant decrease of the F 1s peak, indicating that some protein was adsorbed onto the plasma modified surface. The exposure of PTFE to an oxygen plasma leads to virtually no grafting. XPS results show that there is less than 1% of oxygen on the surface after the treatment. A strong increase in the chamber pressure was observed during the treatment, and optical emission spectrometry reveals the presence of CO, CO@sub 2@ and F in the gas phase, indicating a strong etching of the surface. Depending on the plasma power, water contact angles as high as 170 deg. could be obtained, indicating a super-hydrophobic behaviour, and new surface structures were observed by AFM. At high power, a strong increase in roughness is evidenced, together with the formation of a regular structure. According to the Cassie Baxter model, this increase of roughness is responsible for the super hydrophobic behaviour. Lower amounts of BSA adsorption were detected on high power oxygen plasma-modified PTFE samples compared to nitrogen plasma-modified PTFE samples. @FootnoteText@ @footnote 1@ N. Vandencasteele, D.H. Fairbrother, F. Reniers. Plasma processes and polymers 2, 493-500, (2005).

8:20am **PS1+BI-ThM2 Patterning of Plasma Polymers for Bioarrays***, **G. Mishra**, S.L. McArthur,* University of Sheffield, UK

Protein arrays are solid-phase ligand binding assay systems. They require the immobilisation of proteins on a range of surfaces which include glass, Si wafers and a range of polymers. The assays are highly parallel (multiplexed) and often miniaturised (microarrays, protein chips). Their advantages include being rapid and automatable, capable of high sensitivity, economical on reagents, and giving an abundance of data for a single experiment. Plasma polymerisation presents a versatile approach to surface modification of these devices. The range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple coatings with specific properties are required for a single device. This project investigates the use of plasma polymerisation to produce arrays with a range of chemical functionalities. The ability to spatially define reactive regions is integral to the project. The challenge lies in simultaneously obtaining high spatial and chemical resolution. In this study we use a range of patterning techniques including photolithography and physical masks and compare the resultant pattern resolution and chemical functionality using XPS, ToF-SIMS and AFM. The results highlight the complexities introduced by the gas phase deposition process and the undercutting that can occur with the physical masks. The issue of compatibility of reactive plasma polymers with the photolithographic process is an important aspect under scrutiny. Our results suggest that complex multilayer layered plasma coatings can be produced without compromising chemical properties of deposits.

8:40am **PS1+BI-ThM3 Plasma Polymerized Thin Films for Tailored Interaction with Human Blood and Cells***, **C. Oehr**,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany **INVITED**

Plasma Polymerization is used since for more than four decades to develop thin films for different kinds of applications. At least since the seventies of the last century application of these films is mentioned in the fields of medicine and pharmacy. Due to the fact that polymers are used to design low-weight devices and to realize different geometries very easily, the films are mainly deposited onto polymeric substrates. It is a characteristic property of plasma polymerized films to show strong adhesion onto this materials due to the creation of chemical bonding between film and substrate. Such thin layers with good adhesion, a defined amount of chemical functionalities and stability to sterilization processes are generated and fulfill the needs for medical application. The interaction of biological systems with materials can be divided in three subsystems. First, the interaction with bio-molecules. Here the binding of molecules with specific activities on one hand and the minimizing of unspecific protein adsorption on the other hand can be influenced by thin plasma polymers deposited on medical devices. Second, the interaction of bacteria can be modulated via depositing of thin films with bacteriostatic or bacteriocidic properties on devices. Third, the interaction of mammalian cells can also be influenced to enhance the cell growth and proliferation for the development of test kits or implants. In the talk examples of the first and the third category will be given. Beside the preparation of the mentioned films also the analytic tools necessary for film development and control of its properties are stressed in this contribution. A correlation between physico-chemical properties of the applied plasma polymerized films and the biological requirements will be given.

9:20am **PS1+BI-ThM5 RF(13.56MHz) Glow Discharges fed with Acrylic Acid and Allylamine vapours to obtain Functional Coatings for Biomedical Applications***, E. Sardella, **P. Favia**, L. Petrone, M. Nardulli,* University of Bari, Italy*; R. Gristina,* IMIP-CNR, Italy*; R. d'Agostino,* University of Bari, Italy

Today, a broad range of plasma processes is used to control cell adhesion and growth on biomaterials for tissue engineering and manufacturing of biomedical devices. N-@footnote 1@ and O-@footnote 2@ groups are considered very attractive because they are able to improve cell adhesion and function as "anchor" sites for biomolecules immobilization.@footnote 3@ In this work plasma deposition of acrylic acid (AA), allylamine (AAm) vapours and their plasma co-polymerization have been carried out to deposit functional coatings for several kind of biomedical applications. In particular AA/AAm co-polymerisation can provide different "anchor" sites usable for grafting biomolecules with different activities (ex. antibacterial vs. eukaryotic cell-adhesiveness) on the same substrate. Moreover, these coatings can exhibit zwitterionic characteristics in water and they may find utility in the separation of proteins from solution. A correlation between surface diagnostic analyses (XPS, WCA, FTIR) and plasma phase characterizations (AOES) allowed to provide a correlation between relative density trends of the emitting species in the plasma and the chemical-physical properties of the modified substrate. A titration with water solutions at different pH allowed picking out acid/base properties of the films that can render them very attractive both as supports for cell adhesion and as "smart"materials in drug delivery approaches. In vitro cell culturing of 3T3 fibroblast cell line, were performed to assess the ability of such kind of coatings to influence cell adhesion and growth. Acknowledgements MIUR-FIRB RBNE012B2K is gratefully acknowledged for the financial support. @FootnoteText@ @footnote 1@A. Harsch et al. Journal of neuroscience methods, 2000;98:135-144@footnote 2@Detomaso et al. Biomaterials 2005; 26-18: 3831-3841@footnote 3@D.A. Puleo et al. Biomaterials, 2002;23:2079-2087.

10:20am **PS1+BI-ThM8 Fabrication of High Density and High-Aspect Silicon Nano-column Using Neutral Beam Etching and Ferritin Iron Core Mask***, **S. Saito**, T. Kubota,* Tohoku University, Japan*; T. Matsui,* Matsushita Electric Industrial Co., Ltd., Japan*; Y. Uraoka, T. Fuyuki,* Nara Institute of Science and Technology, Japan*; I. Yamashita,* Matsushita Electric Industrial Co., Ltd. and Nara Institute of Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

Semiconductor devices has been getting smaller and following Moore's Law. The design rule, the smallest line width, of these devices will be less than 50 nm nanometers within the next decade. Conventional optical lithography process has a theoretical limit to draw patterns smaller than the light wavelength and finer processing techniques are now being intensely surveyed but no methods meet the requests for mass nano-structure production. In order to breakthrough this limit, we have already

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

proposed a new method to fabricate 7 nm nano-dots using the ferritin iron-core as an etching mask and Cl neutral beam for Si etching processes. The ferritin is one of the proteins and has a spherical protein shell with a cavity of 7 nm diameter. It can biomineralize iron as hydrated iron oxide in the cavity and store it in vivo. The Cl neutral beam could realize high etching anisotropy and high etching selectivity to ferritin iron-core without any radiation damages. In this study, we also tried to fabricate higher density and high-aspect Si nanocolumn structure using high-density array of ferritin iron core. The ferritin array could be made just over thin SiO@sub 2@ film (~3nm thick) on Si substrate. In this condition, however, the diameter of Si nanocolumn was enlarged to 14 nm and the etching profile had a slight taper because of extremely low SiO@sub 2@ etching rate using Cl neutral beam. To overcome the problem, we tried two-step neutral beam etching process. For quickly etching the surface SiO@sub 2@, F neutral beam was used. After that, the bulk Si was etched with high anisotropy using Cl neutral beam. As a result, for the first time, the diameter of Si nanocolumn could be shrunk with keeping highly anisotropic etching profile even at narrow space of less than 6nm. This study was supported by Leading Project of Ministry of Education, Culture, Sports, Science and Technology.

10:40am **PS1+BI-ThM9 The Influence of Bond-Coating on Plasma Sprayed Alumina-Titania, Doped with Biologically Derived Hydroxyapatite, on Stainless Steel**, ***S. Salman***, *B. Cal, O. Gunduz,* Marmara University, Turkey; *S. Agathopoulos,* Ioannina University, Greece; *F.N. Oktar,* Marmara University, Turkey

The influence of bond-coating on the quality of thin coatings (~100 µm) of alumina-titania (60%-40%), doped with 5% and 10% bovine hydroxyapatite, plasma-spayed on stainless steel (316), was experimentally investigated by measuring the tensile strength and the ratio of adhesive/cohesive strength of the coatings. The bond-coating layer was alumina-titania (60%-40%). The experimental results (mainly the values of the ratio adhesive/cohesive strength and the microstructure of the coating layers) and their discussion in the light of earlier similar studies show that bond-coating process can result in coating composite structures of high quality, which is of high importance for devices used in biomedicine.

Plasma Science and Technology
Room 2011 - Session PS2-ThM

Plasmas and Polymers

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

8:00am **PS2-ThM1 Tuning Polymer Surfaces by Cold Plasma Technology**, ***R. d'Agostino***, University of Bari, Italy **INVITED**

Polymers modification by means of low pressure plasma processes for different applications are currently investigated in the University of Bari and in the spin off Plasma Solution. Our research follows several applicative directions, however while in the University we mostly deal of fundamental issues, in the spin off we aim to develop industrial customized processes and plasma reactors. Our traditional approach for studying plasma modification of polymers is generally based on a combined use of plasma and surface diagnostics. This, along with performance analyses, allows often to set proper on-line diagnostics for process control and to tune the morphology/composition/performance of treated polymers. The issues covered in the talk include some of our best processes as transparent barrier coatings, nano- and micro-structured polymer films, super-hydrophobic materials, non fouling, corrosion protection, tissue engineering, bacterial resistant coatings, atmospheric pressure glow discharges for Teflon-likes.

8:40am **PS2-ThM3 Morphological and Chemical Evolution of Model Resist Polymers for Plasma/Energetic Beam Templating Materials***, *R. Phaneuf,* ***T. Kwon***, *R.L. Bruce, S. Engelmann, G.S. Oehrlein,* University of Maryland; *B. Long, G. Willson,* University of Texas, Austin; *D.B. Graves, D.G. Nest, M. Goldman, J. Vegh,* University of California, Berkeley; *A. Alizadeh,* GE Electric Global Research Center

The control of the line edge / surface roughness induced by plasma etching, one of the essential process steps in IC fabrication, may ultimately limit the minimum critical dimensions obtainable in nanoscale-devices. This issue is thus crucial in the development of the new generation of organic mask materials for advanced lithographic techniques. In the work presented here we have investigated the evolution of surface roughness of five prototypical resists, polystyrene (PS), poly (4-methylstyrene), poly-@alpha@-methylstyrene (P@alpha@MS), poly-3-hydroxy-1adamantyl methacrylate (HAMA), and poly-3-hydroxy-1-adamantyl acrylate (HAdA), during inductively coupled plasma (ICP) etching with O@sub 2@, with Ar, and with C@sub 4@F@sub 8@/90%Ar plasmas. Our AFM measurements show a strong correlation of the rate of roughening of these resists with type and position of chemical functional groups, the tendency toward chain scission vs. cross-linking in the presence of ionizing radiation, and with the composition of the etching gas. In particular, we find that for the C@sub 4@F@sub 8@/90%Ar plasma, poly (4-methylstyrene) shows the smallest surface roughness among all the samples, and HAMA the highest. We compare the morphological and chemical changes of these model resists under plasma etching to the extreme case of ion sputtering during Ar@super +@ beam bombardment. *Work supported by the National Science Foundation under NIRT, # CTS-0506988.

9:00am **PS2-ThM4 Advanced Plasma Polymerization Methods to Deposit Multifunctional Coatings**, ***D. Hegemann***, *M.M. Hossain, D.J. Balazs,* Empa, Swiss Materials Science & Technology, Switzerland

Products made with the help of flexible porous webs, e.g. textiles, become more and more sophisticated and 'multifunctional'. Tailored surface modifications are required to meet customer needs and to assure a share in the market. However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of waste water. Plasma polymerization, on the other hand, as a dry and eco-friendly technology, is offering an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fibers. At the same time, the bulk properties as well as the touch of the textiles remain unaffected. Of great potential are nanoporous plasma coatings which can be achieved by adjusting the deposition/etching conditions at the growing film surface. Depending on functional groups incorporated during the plasma polymerization process, permanent hydrophilic surfaces can be achieved which are mechanically stable. Moreover, dye molecules can be attached to the accessible functional groups within the plasma coatings, thus enabling substrate independent dyeing of textiles. Different other molecules might be added as well, e.g. biomolecules for enhanced cell growth. Co-sputtering of silver during plasma polymerization enables the controlled incorporation of Ag nanoparticles into a functional plasma polymer matrix in a one-step process inducing an antimicrobial activity. Hence, nanostructured, multifunctional textile surfaces can be achieved. However, suitable plasma reactors and scalable processes are required for an economical treatment of textiles. The scale-up of plasma processes is thus an important issue and is demonstrated using a continuous web coater.

9:20am **PS2-ThM5 Low Temperature PECVD of Silicon Oxynitride Thin Films from Dimethylaminosilanes: Role of Oxygen Addition**, *R. Di Mundo, F. Fracassi,* ***R. d'Agostino***, University of Bari, Italy; *F. Palumbo,* IMIP-CNR

Silicon oxynitride (SiON) coatings are important materials as dielectrics and optical components. So far attempts to replace hazardous silane in SiON PECVD processes with organosilicon precursors have led to organic SiC@sub x@N@sub y@O@sub w@H@sub z@ films. However, considering the good features of SiN coatings deposited at low temperature from inductively coupled discharges fed by bis(dimethylamino)dimethylsilane (BDMADMS) and argon,@footnote 1@ we tested the addition of O@sub 2@ to this novel system for SiON films deposition. The O@sub 2@-to-monomer ratio was varied at low and high input power until transition to oxide was observed. The chemical composition of the coatings was characterized by means of FT-IR and XPS analyses while a deep investigation on the plasma phase was carried out by Optical Emission Spectroscopy (OES) in order to gain insight into the role of oxygen atoms in the deposition mechanism. Results indicate that at high input power and low O@sub 2@-to-BDMADMS ratio highly inorganic SiON films can be obtained. The sharp increase of the O/Si ratio in the coating, as the O@sub 2@ concentration in the feed rises, is accompanied by a significant reduction of the N/Si ratio, which is even faster than the decrease of the C/Si ratio. This particular chemical evolution can be correlated with the trends of relative density in plasma phase of N-containing species (NH, CN) as well as of oxidation products (CO, OH) detected with OES, suggesting some favourite reaction paths within the process.@FootnoteText@@footnote 1@R. Di Mundo, R. d'Agostino, F. Fracassi, F. Palumbo, Plasma Process. Polym., 2, 612-617 (2005).

9:40am **PS2-ThM6 Plasma-Assisted Growth of Moisture Diffusion Barriers on Polymers: From Chemical Vapor Deposition to Atomic Layer Deposition***, **M. Creatore**, E. Langereis, I. Volintiru, A. Milella,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Polymer- based technologies are rapidly growing in fields such as flexible solar cells and OLEDs, but long-term stability devices are desired and, therefore, high moisture diffusion barrier films are required (water vapor transmission rates (WVTRs) as low as 10@super -6@ g/m@super 2@day). Sputtering and plasma-enhanced chemical vapor deposition (PE-CVD) are the most investigated technologies for the deposition of barrier films, although only µm-thick multi-layer systems appear to meet the above-mentioned requirements. Very recently, however, Atomic Layer Deposition (ALD) has been addressed as an attractive route towards excellent and thinner barriers. Also in this case, plasmas can assist the growth (plasma assisted ALD, PA-ALD) by providing a radical source, which replaces one (molecular) deposition precursor (e.g., O radicals replacing H@sub 2@O for Al@sub 2@O@sub 3@ deposition). Here we address the PA-ALD deposition of Al@sub 2@O@sub 3@, consisting of cycles of trimethylaluminum dosing alternating with O@sub 2@ plasma exposure. WVTR values as low as 0.005 g/m@super 2@day are reported for thin (20 nm) PA-ALD Al@sub 2@O@sub 3@ on polyesters, while 100 nm- thick oxides (SiO@sub 2@ and Al@sub 2@O@sub 3@) deposited by means of PE-CVD in a remote plasma configuration are characterized by WVTR values of 0.15 g/m@super 2@day. The superiority of the PA-ALD layers is attributed to the control of the film microstructure during the growth: chemical (XPS), optical (spectroscopic ellipsometry) and morphological (atomic force microscopy) analyses have pointed out towards lower hydrogen content-, higher refractive index- and smoother PA-ALD films in comparison with PE-CVD layers. Routes for the microstructure control in PE-CVD will be also addressed: ion bombardment (via an external rf bias), in terms of ion energy and ion-to-radical flux ratio, was found to be a key parameter in tuning the film microstructure and improving the moisture permeation barrier properties.

10:00am **PS2-ThM7 Super-Hydrophobic Transparent Polymer Surfaces Fabricated by Plasma Etching and Deposition***, **N. Vourdas**, M.E. Vlachopoulou, A. Tserepi, E. Gogolides,* Institute of Microelectronics, NCSR Demokritos, Greece

Wettability control is of great importance in many industrial and scientific areas; from manufacturing of water repellent surfaces to droplet frictionless motion in microfluidics, and biocompatibility tuning. Wetting or repellent behavior is governed by both surface chemistry and topography. In particular, super-hydrophobicity is attained by combining low surface energy coatings and high-aspect-ratio (HAR) geometrical characteristics. Liquids contact only the upper part of HAR surfaces (Cassie-Baxter regime). In this study we present a novel, simple, generic and fast technique to fabricate stable super-hydrophobic, yet transparent surfaces by means of high-density plasma etching and deposition.@footnote 1@ An Inductively Coupled Plasma (ICP) reactor is used to treat two different kind of polymers; an organic one (PMMA) and a hybrid one (PDMS). Different plasma chemistries pertinent to each polymer are implemented to etch the surfaces followed by a fluorocarbon deposition to control the surface roughness and the surface chemistry respectively. AFM is used to characterize morphology and water contact angle (CA) and CA hysteresis to characterize wetting properties. We demonstrate high aspect ratio pillars with height ranging from ca. 350nm to several microns depending on the processing time, and contact angles of 150@super o@ with hysteresis lower than 15@super o@. Surfaces with pillar height less than 400nm are also transparent. @FootnoteText@@footnote 1@Greek Patent application number 20050100473; PCT application number GR2006/000011.

10:20am **PS2-ThM8 Fabrication and Characterization of Plasma Processed Surfaces with Tuned Wettability***, **P. Colpo**, A. Ruiz, L. Ceriotti, A. Valsesia, F. Brétagnol, G. Ceccone, D. Gilliland, F. Rossi,* European Commission, Institute for Health and Consumer Protection, Italy

Plasma treatments have been extensively applied to polymers, metals or elastomers for fabricating engineered surfaces. Among others, applications of plasma processing include the alteration of the wetting properties of surfaces to create either hydrophilic or hydrophobic surfaces. The wettable behaviour of surfaces is determined by several parameters, being the surface energy and the surface roughness the most important ones. Tailoring the roughness of surfaces has been proved to be an effective method for enhancing its hydrophilic or hydrophobic character. Therefore, studying the wetting capacity of rough surfaces has attracted special interest in the last years. In this scope, we have used a combination of plasma processes including etching and polymerization to prepare rough surfaces with different hydrophilic/hydrophobic character. The surfaces have been then analysed in terms of chemistry, roughness and wettability. Surfaces with different roughness have been fabricated by etching with several gases and different treatment duration a layer of polymer resin deposited on silicon and glass substrates. The etched surfaces were analysed by XPS, ToF-SIMS, SEM, and the results were compared with the wettability and roughness, given by contact angle and surface profile measurements respectively. We found a correlation between the contact angle, i.e. the hydrophilic character, the roughness and the chemical composition of the surface. Teflon-like, acrylic acid and PEG layers were deposited on the rough plasma treated surface by plasma polymerisation. Selected wettability has been achieved combining plasma etching and plasma deposition processes. Superhydrophilic and superhydrophobic surfaces have been obtained with a fast, easy to implement method, which has also the advantage of mass production, repeatability and reliability. The surfaces fabricated have interest in a variety of applications (coatings, medical devices, biosensors, ...).

10:40am **PS2-ThM9 Plasma-Polymerised Surface Chemical Gradients as Platforms for Making Biomolecule Gradients***, **D.E. Robinson**, R.D. Short, D.J. Buttle,* University of Sheffield, UK*; T. Day, A. Marson,* University of Manchester, UK*; K. Parry,* Plasso Technology

A continuous variation in a surface chemical feature (i.e. a gradient) is important in controlling a variety of processes, biological@footnote 1@ and chemical.@footnote 2,3@ The production of such features on the millimetre and sub-millimetre scale length on a material surface is a challenge, and the methods employed currently are only suitable for one-off experiments. Gradients of chemical functionalities may be fabricated by plasma polymerisation, using a moving slot, to separate plasma from the collecting substrate (and simultaneous control of two monomer gas ratios).@footnote 4@ This method offers advantages over others, vis-a -vis the robust (stable) nature of the gradients, and the scalability of the method, an exact precision in the start and end point and shape of the gradient, gradients can be fabricated onto a wide range of substrates, e.g. plastics, glass and metals. A gradient of functional heparin (a gylcosaminogylcan(GAGs)) is fabricated by depositing a plasma-polymerised gradient of allyl amine (the co monomer is octadiene). A gradient of plasma-polymerised allyl amine is incubated with native heparin, forming a functional gradient. Functionality is demonstrated by binding of known heparin-binding proteins.@footnote 5@ Gradients of GAGs are important in functional diversity, playing fundamental roles in biological processes such as blood clotting, tissue structure and organisation, development and morphogenesis and many disease processes. The fabrication of a heparin gradient provides an important research tool by which some of these processes can be studied in vitro. @FootnoteText@ @footnote 1@N L Jeon, K W Dertinger, G M Whitesides, et al., Langmuir 2000, 16, 8311@footnote 2@J Aizebnberg, A J Black, G M Whitesides, Nature 1999, 398, 495 @footnote 3@B S Gallardo, V K Gupta, et al., Science 1999, 283, 57 @footnote 4@J D Whittle, D Barton M Alexander, R D Short, Chem. Comm., 2003, 14, 1766 @footnote 5@D J Mahoney, A J Day, R D Short et al., Anal. Biochem. 2004, 330, 123-129.

Manufacturing Science and Technology
Room 2018 - Session MS-ThA

Sensors, Metrology, and Control

Moderator: A.C. Diebold, SEMATECH

2:00pm **MS-ThA1 Three-dimensional Imaging of Nano-Voids in Copper Interconnects using Incoherent Bright Field Tomography**, *P. Ercius, M. Weyland,* Cornell University; ***D.A. Muller,*** Cornell University, US; *L.M. Gignac,* Thomas J. Watson Research Center **INVITED**

As integrated circuits have shrunk, conventional electron microscopies have proven inadequate for imaging complicated interconnect structures due to the overlap of features in projection. These techniques produce transmission functions with a non-monotonic dependence of intensity on thickness for common microelectronic materials, making them unsuitable for tomography. We report the use of an incoherent bright field imaging technique in a scanning transmission electron microscope optimized for the three-dimensional reconstruction of thick copper microelectronic structures. Predictable behavior of the signal in samples up to ~1 micron thick allows us to reconstruct and quantify the shape and volume of stress voids within Ta-lined interconnects as well as analyze the liner roughness in 3 dimensions.

2:40pm **MS-ThA3 Critical Dimension Metrology: A Comprehensive Evaluation of Current Techniques in Spectroscopy-Based Scatterometry**, ***C. Saravanan***, *Z. Liu,* Nanometrics Inc

In recent years scatterometry has evolved into a reliable, non-invasive and fast technique to characterize critical dimensions (CD) in semiconductor device fabrication. Both polarized-light Normal Incidence Spectroscopy (NIS) and Spectroscopic Ellipsometry (SE) have been successfully used as competing techniques in CD metrology. While several studies have been performed to evaluate these techniques, a thorough evaluation of the 'optimal space' of applicability for these individual techniques does not exist. Furthermore, very little is known about the combined NIS and SE approach as an alternate method for CD metrology. In this paper we first explore 'regions' of optimal applicability of these three techniques (NIS, SE and NIS+SE) by performing simulations on multiple structures with varying heights, sidewall angles, optical properties and pitch (360nm, 180nm, 90nm, 45nm, 32nm and 16nm). We show that regions of optimal applicability exist for all three techniques. We also perform experimental studies for some typical applications and demonstrate the benefit of using combined analysis of NIS and SE to limit parameter correlation and to enhance sensitivity. This is particularly important for scatterometry applications in future technology nodes with much smaller device dimensions.

3:00pm **MS-ThA4 Low Coherence Optical Intereferometry and Raman Scattering Spectroscopy for Stress Tensor Measurements**, ***W.J. Walecki,*** *T. Azfar, A. Pravdivtsev, A. Koo, J. Ryu,* Frontier Semiconductor

In this paper we discuss accuracy and reproducibility of two techniques for metrology of stress tensor in semiconductor wafers: novel combined IR low coherence optical interefermetry@footnote 1@ allowing simultaneous measurement of wafer topography and wafers and thin film thicknesses, enabling calculation of all in plane stress tensor components, and high precision tensor resolved Micro-Raman spectroscopy. Typical micro-Raman measurements are performed in backscattered geometry. Observed stress dependent Stokes shift is related to stress in the material using specific stress tensor model typically derived on a basis of symmetry considerations,@footnote 1,2@ the usual reported reproducibility of the stress measurement of the order of 10 MPa-30 MPa,@footnote 2,3@ which corresponds to reproducibility of the Stokes shift of the order of 0.05 cm-1). By applying very large focal length grating spectrometer (effective focal length 1.34 m), and proprietary thermal drift compensation we were able to achieve thermal stability of the better than 0.0002 cm-1 / min which allows us to further improve reproducibility. We also propose two methods for recovering three and six stress tensor components in cubic crystals (such as Si/SiGe) on microscopic scale. @FootnoteText@ @footnote 1@ W.J.Walecki, A. Pravdivtsev, K. Lai, M. Santos, G. Mikhaylov, A. Koo, in ''Characterization and Metrology for ULSI Technology 2005'', edited by D.G. Seiler, et al, American Institute of Physics, p. 338- 342, 2005@footnote 2@ V. T. Srikar, A. K. Swan, M. S. Unlu, B. B. Goldberg, and S. M. Spearing, IEEE Journal of Microelectromechanical systems, Vol. 12, No. 6, December 2003, pp. 779-787@footnote 3@ Ingrid De Wolf, Chen Jian, W.Merlijn van Spengen, Optics and Lasers in Engineering 36 (2) (2001) pp. 213-223.

3:20pm **MS-ThA5 Micro-Probe CV and IV Analysis of Thin Dielectric Films in Product Wafer Scribe-Line Structures**, ***V.V. Souchkov,*** *T.M.H. Wong, V.N. Faifer, M.I. Current,* Frontier Semiconductor

A 50 µm metal probe has been coupled with pattern recognition optics and a precision stage for automated CV and IV testing of dielectric layers in scribe-line test structures on IC product wafers. Highly repeatable contact conditions are obtained though the use of a MEMS-based torsion balance spring mounting which provides capacitance measurements within 0.1% for repeated landings of the probe. High repeatability capacitance measurements provide for correspondingly high quality determination of dielectric characteristics, EOT, Vfb, Dit, Na and Qeff, from CV analysis. Dielectric leakage and breakdown characteristics, including Vbd, Qbd and TTBD, can be obtained for positive and negative ramped bias conditions. Examples of dielectrics include thin (1 nm) SiO@sub 2@, oxy-nitrides and Hf-based oxides as bare films and incorporated in capacitor structures.

3:40pm **MS-ThA6 Characterizing Copper Lines for Advanced Interconnect Using Normal Incidence Scatterometry**, ***Z. Liu,*** *Y. Hao,* Nanometrics Inc.

With the continuous evolution of smaller device dimensions and denser circuit integration, copper interconnect with low-k dielectrics have been the most popular solution for future technology generations. In copper interconnect, one of the major challenges is the dimensional control of the interconnect features, which is critical to achieve necessary circuit performance of the device. To achieve best device performance, there is limited tolerance of the profile variation in interconnect structures. This dimensional control requirement demands metrology solutions to characterize the interconnect structures in all metal levels. In this paper we propose to use normal incidence scatterometry to characterize the copper lines (line width and height) at various metal levels. Normal incidence scatterometry uses a polarized broadband light source to measure the reflectance spectrum of the grating line structure. Using the modeling technique, profile information including line width and height can be determined. In this work we measure copper grating line structures at different metal levels (M1, M3 and M7) after each chemical mechanical polishing. These structures correspond to different copper line-widths ranging from 0.09 to 0.8 um. Structures with copper lines either parallel or perpendicular to each other between adjacent metal levels are studied. Advanced modeling techniques are used to decouple spectral contributions between the top metal level and the metal levels below. The measurement results are compared with results from other reference techniques, e.g. X-SEM and a very good agreement is demonstrated.

4:00pm **MS-ThA7 Leakage Current and Dopant Activation in Ultra-Shallow Junctions Following Ms-Anneals Measured by Non-Contact Junction Photo-Voltage Methods**, ***V.N. Faifer,*** *T.M.H. Wong, M.I. Current,* Frontier Semiconductor

Leakage current and dopant activation characteristics of ultra-shallow junctions formed with ms-timescale anneals, which provide the beneficial result of minimal dopant diffusion, are highly sensitive to damage accumulation effects during the implantation of dopants, pre-amorphizing and various cocktail (C, F, S, etc.) ions. Damage accumulation levels are a result of the choice of ion, energy, dose and target material as well as process conditions such as beam current density, wafer temperature and beam scanning details for each implant cycle. The residual damage levels after annealing depend on the depth and character of the accumulated damage and the time-at-temperature ramp and ambient atmosphere conditions during each annealing step. For ms-timescale anneals which involve the use of scanned and pulsed energy deposition, the uniformity of the dopant activation and damage annealing process is strongly dependent on the spatial extent and overlap strategies used for the energy deposition beam used for heating. Measurement of junction characteristics through analysis of surface photo-voltage levels provides non-contact, high precision and independent measures of sheet resistance and leakage current density over 4 orders of magnitude. Discussion of leakage current effects will include the impact of background doping and defect density on carrier recombination and trap-assisted tunneling mechanisms. High-resolution (1,000 points per wafer) mapping of sheet resistance and leakage current variations provides rapid feedback for process evaluation of implant and annealing process equipment and correlation of conditions which result in favorable dopant activation and damage annealing.

Plasma Science and Technology
Room 2009 - Session PS1-ThA

Plasma Processing for High-K/III-V's and Smart Materials

Moderator: J. Margot, Université de Montréal, Canada

2:00pm **PS1-ThA1 Mechanisms and Selectivity for Etching of HfO@sub 2@ and Si in BCl@sub 3@ Plasmas***, **C. Wang**, V.M. Donnelly,* University of Houston

We have investigated etching of HfO@sub 2@ and poly-Si in BCl@sub 3@ plasmas as a function of substrate temperature (T@sub s@), source power, and substrate bias. The etching rates of both HfO@sub 2@ and poly-Si increase with increasing T@sub s@. An activation energy of 4.7 kJ/mol is obtained from an Arrhenius plot of HfO@sub 2@ etching rate vs. T@sub s@. This activation energy is much lower than the heat of vaporization of HfCl@sub 4@ (100 kJ/mol), hence desorption of this product is not rate limiting. The most likely mechanism is one in which the surface, disordered by ion bombardment, is terminated with Hf-O-BCl@sub 2@ and Hf-Cl groups. Etching is limited by chemical sputtering of this chemisorbed layer. Higher T@sub s@ modestly increases the rate at which reactions occur during ion "thermal" spikes. Similarly, the desorption of SiCl@sub 4@ is not limited by the vapor pressure of this product, which is orders of magnitude higher. The etching rate of Si in BCl@sub 3@ plasmas has an activation energy of 3±1 kJ/mol. Consequently, a small improvement in HfO@sub 2@ selectivity over Si can be realized at high temperature. At high (inductively coupled) power, a relatively thin BCl@sub x@ film (detected by vacuum-transfer to an XPS chamber) forms on partially etched HfO@sub 2@ and Si. At low (capacitively-coupled) power, a similar thickness films is present on HfO@sub 2@, but a much thicker BCl@sub x@ film is present on Si. BCl@sub 3@ dissociates in the plasma to yield Cl and BCl@sub 2@ at low power, and additionally, BCl, B, and Cl at high power. Apparently, the rate of BCl@sub x@ deposition on Si does not increase, or increases less than the rate of etching of Si as power increases, perhaps due to a lower sticking coefficient of BCl, compared to BCl@sub 2@, and the enhanced Cl flux. The BCl@sub x@ film formed on the Si surface likely inhibits the formation and sputtering of volatile SiCl@sub x@ species. Supported by SRC and AMD Inc.

2:20pm **PS1-ThA2 Plasma Etching of HfO2 in High-Density Chlorine-Containing Plasmas without RF Biasing***, **K. Nakamura**, K. Osari, D. Hamada, K. Eriguchi, K. Ono,* Kyoto University, Japan

As ultra large scale integrated circuit dimensions continue to be scaled down, high dielectric constant (high-k) materials such as HfO@sub 2@, ZrO@sub 2@, and Al@sub 2@O@sub 3@ are being required as gate dielectric to maintain the gate capacitance in smaller size. For the fabrication of high-k gate stacks, a better understanding of the etching characteristics and mechanisms is indispensable for high-k dielectrics. We have investigated the etching of high-k materials of HfO@sub 2@ using high-density chlorine-containing plasmas excited by electron cyclotron resonance. Experiments were performed in BCl@sub 3@/Cl@sub 2@ gas mixtures at a pressure of 5 mTorr without rf biasing. In pure BCl@sub3@ plasma, some deposition was found to occur on HfO@sub 2@ surface to inhibit etching. By adding Cl@sub 2@ to BCl@sub 3@, the deposition was suppressed to result in etching of HfO@sub 2@. The HfO@sub 2@ etch rates increased with increasing Cl@sub 2@ concentration ratio, and the maximum HfO@sub 2@ etch rate was ~100 nm/min at 60% Cl@sub 2@ addition. At the Cl@sub 2@ concentration ratio in the range 25-50%, the HfO@sub 2@ etch rate was more than 20 nm/min, while the Si etch rate remained almost zero, thus giving extremely high selectivity over Si. In addition, by adding a small amount of O@sub 2@ to BCl@sub3@/Cl@sub 2@, the HfO@sub 2@ etch rate was further enhanced. The maximum HfO@sub 2@ etch rate was ~150 nm/min at 5% O@sub 2@ addition to BCl@sub 3@/60%-Cl@sub 2@ plasma, while the Si etch rate also increased to deteriorate the selectivity over Si down to 4. These results were compared with plasma and surface diagnostics, to understand plasma-surface reaction mechanisms responsible for selective etching of HfO@sub 2@.

2:40pm **PS1-ThA3 Effects of Low Energy Nitrogen Plasma on the Removal of HfSiON***, **W.S. Hwang**,* National University of Singapore*; W.J. Yoo,* Sungkyunkwan University, Korea, Singapore*; B.J. Cho, D.S.H. Chan,* National University of Singapore

HfSiON high-k dielectric is being studied extensively to improve the electrical properties of conventional SiON dielectric since it can attain low leakage current especially for low standby power application. The removal of high-k dielectric using a wet etching technique is more frequently used than dry etching techniques which result in poor etching selectivity over underlying Si. Dilute hydrofluoric acid (DHF) solution etches amorphous HfSiON easily without the loss of the underlying Si. However, crystallized HfSiON shows strong resistance in DHF after post-deposition anneal, posing challenges in the integration involving the removal of high-k dielectric at the active transistor regions of source and drain. In this work, the DHF wet removal of HfSiON assisted by N@sub 2@ ion bombardment is investigated. The anisotropic and undercut-free profile is achieved by this technique. An as-deposited amorphous HfSiON of 4 nm can be removed by 1% DHF in 15s, whereas the annealed crystallized HfSiON cannot be removed. N@sub 2@ plasma treatment helps the crystallized HfSiON to be etched in DHF. The ion assisted wet removal is made feasible via changing the structure of the crystallized HfSiON to the mixture of metallic Hf and amorphous HfSiON. We found a correlation between ion energy and formation energy of HfSiON; the ions having energy less than 9eV do not penetrate HfSiON, whereas ions having energy higher than its formation energy of ~ 9.3eV penetrate HfSiON and participate in the formation of SiN. The low energy ion assisted wet removal method results in lower threshold voltage than the conventional DHF wet etching method which causes lateral encroachment of HfSiON that lowers gate oxide capacitance. This plasma assisted method can be applied extensively to various removals of high-k material constrained by low crystallization temperature and thereby high etching resistance in conventional DHF.

3:00pm **PS1-ThA4 Vacuum-Ultraviolet Induced Photocurrents in Plasma-Charged, Atomic Layer Deposited, HfO2/SiO2/Si Dielectric Stacks****, G.S. Upadhyaya**, J.L. Shohet,* University of Wisconsin-Madison

Advanced MOS technologies currently utilize gate oxides so thin that any further decrease in silicon-oxide thickness results in a large increase in power consumption due to high gate-leakage current. High-K dielectric materials are being investigated in order to maintain high coupling capacitance and limiting the leakage current by using thicker gate-oxide layers. In this work, we utilize the high-K dielectric hafnium oxide because of its resistance against silicide formation. It is well known that plasma and vacuum-ultraviolet (VUV) radiation-induced damage during fabrication adversely affects device reliability by degrading the gate oxide. The VUV-radiation response of hafnium oxide is relatively unknown. To this end, we investigate the effect of VUV radiation with energies from 7 to 21 eV, which is the range of energies emitted by most processing plasmas, on uncharged as well as plasma-charged, atomic-layer deposited (ALD) HfO2/SiO2/Si dielectric stacks. The electron-storage ring at the University of Wisconsin Synchrotron Radiation Center will be used as the VUV source. By measuring the substrate and photoemission currents during irradiation and the resulting surface potential, information about the nature of traps and rate of interface state generation in dielectric layers as a function of photon energy can be obtained. Comparison of HfO2 with SiO2 dielectric layers shows that, due to the lower bandgap of HfO2, traps and interface states in HfO2 are populated at a lower VUV photon energy than for silicon oxide. This indicates that charging of HfO2 during processing may occur more easily than for SiO2. @FootnoteText@ *Worksupported by the National Science Foundation under grant No. DMR-0306582. The UW-Synchrotron is a national facility, funded by the National Science Foundation under grant No. DMR-0084402.

3:20pm **PS1-ThA5 Mechanisms of Plasma-Induced Damage during Ion-Assisted Chemical Etching of Indium-Zinc-Oxide Films in Reactive Plasma Chemistries***, **L. Stafford**, W.T. Lim, S.J. Pearton,* University of Florida*; J.-I. Song, J.-S. Park, Y.W. Heo, J.-H. Lee, J.-J. Kim,* Kyungpook National University, Korea

Because of its good electrical conductivity, wide transmittance window, large work function, excellent surface smoothness, and low deposition temperature, Indium-Zinc-Oxide (IZO) has recently emerged as a very promising material for transparent electrodes in various optoelectronic devices such as liquid crystal displays, light-emitting-diodes, and solar cells. While the growth characteristics of IZO layers are relatively well optimized, the development of a reliable pattern transfer process remains to be examined. In this work, we investigate the potential of Cl@sub 2@ and CH@sub 4@/H@sub 2@ plasma chemistries for the dry etching of IZO films. The influence of the discharge chemistry on the post-etched surface morphology and near-surface stoichiometry is also investigated. While the Cl@sub 2@-based plasma shows little enhancement over physical sputtering in a pure argon atmosphere, the CH@sub 4@/H@sub 2@/Ar chemistry produces a strong increase of the IZO etch rate. The surface morphology of IZO films after etching in Ar and Ar/Cl@sub 2@ discharges is smooth, whereas that after etching in CH@sub 4@/H@sub 2@/Ar presents particle-like features resulting from the preferential desorption of In- and O-containing products. While the etch-induced damage in Ar and

Ar/Cl@sub 2@ plasmas are constrained to the surface vicinity, etching in CH@sub 4@/H@sub 2@/Ar produces a Zn-rich surface layer, whose thickness (~55 nm) is well-above the expected range of incident ions in the material (~1.5 nm). Auger electron spectroscopy measurements as a function of plasma exposure time indicate that diffusion of O, Zn and In atoms upon preferential desorption of volatile O- and In-containing reaction products is responsible for damage formation. A diffusion model accounting for the observed depth profiles is proposed. Such damage of the IZO layer is expected to have a significant impact on the transparent electrode properties in optoelectronic device fabrication.

3:40pm **PS1-ThA6 Reactive Plasma for High Aspect Ratio Etching and Surface Modification*, S.W. Pang,*** The University of Michigan **INVITED**

In this talk, plasma etching of Si, GaAs, and polymer will be reviewed. Depending on the applications, fast etch rate, high aspect ratio etching, and damage-free etching are required. In Si and GaAs etching, fast etch rates have been demonstrated to produce vias by etching through an entire wafer. On the other hand, for devices with nanostructures, high aspect ratio (large height and narrow width) etching is needed to minimize lateral etching. In addition, for these devices to be electrically or optically functional, surface damage due to plasma etching has to be eliminated. Additionally, to remove polymer inside nanochannels of microfluidic systems, fast lateral etching of polymer has been developed. Etch conditions that can provide the desired etch characteristics will be discussed. Finally, surface energy of various materials could be modified by exposure to reactive plasmas. Results of applying plasma surface treatment to reversal nanoimprint will be shown.

4:20pm **PS1-ThA8 Atomic Layer Etching of III-V compounds using a Low Angle Forward Reflected Neutral Beam*, S.D. Park*,** *C.K. Oh, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea

III-V compounds are currently investigated for various electronic and optical devices, due to high electron mobility and high useful temperature range. Therefore, a few researchers have investigated on the dry etching of III-V compounds using halogen-based reactive-ion-etching (RIE). However, these conventional RIE processes lead to physically damage to the surface of the devices, such as creation of surface defect including structural disruption, intermixing layer or stoichiometry modification and the increment of surface roughness, due to the use of energetic reactive ions to achieve vertical etch profiles. Among those dry processes, atomic layer etching (ALET) can be assigned as the most possible method to realize atomic scale etch-rate controllability of III-V compounds without physically damaging to the surface of III-V compounds. In this study, the ALET of III-V compounds were carried out using a sequential Cl@sub 2@ adsorption and a Ne neutral beam irradiation to the surface. By supplying Cl@sub 2@ and Ne neutrals higher than critical doses, the exactly same etch depth per cycle corresponding to one atomic layer per cycle could be obtained by a self-limited etching mechanism. The etched step height was measured using a step profilometer. The measured step height was divided by the total number of ALET cycles to yield the etch rate per cycle. An atomic force microscope (AFM) was used to measure the surface roughness. Also, X-ray photoelectron spectroscopy (XPS) was utilized to analyze the change of composition of III-V compounds.

4:40pm **PS1-ThA9 Improvement of Programming Characteristics of Ge2Sb2Te5 Thin Films by Incorporating SiO2 for Application of PcRAM*,*** *S.W. Ryu,* ***J.H. Oh,*** *B.J. Choi,* Seoul National University, Korea*; S.K. Hong,* Hynix Semiconductor Inc., Korea*; C.S. Hwang, H.J. Kim,* Seoul National University, Korea

In an effort to overcome the scaling limit of the floating gate non-volatile memory (NVM) technology below the 30nm design rule, the semiconductor industry has been forced to find alternative NVM.@footnote 1-4@ Phase change random access memory (PCRAM) attracts great interest not only because it satisfies the various demands for NVM devices but also because its fabrication process is relatively simple. However, the high level of reset current has been the major obstacle for further scaling of PCRAM because of the limited on-current drive capability of the cell transistor (<1mA/µm) and then unexpected crystallization of unstable amorphous state has resulted from low crystallization temperature of Ge @sub 2@Sb@sub 2@Te@sub 5@ (GST). The phase change characteristics of GST films for phase change random access memory devices were improved by incorporating SiO@sub 2@ into the GST film through co-sputtering at room temperature. Isochronal annealing showed an increased resistivity of the crystallized GST films in proportion to the incorporated quantity of SiO@sub 2@ which leads to a reduction in the writing current. Incorporated SiO@sub 2@ also inhibits crystallization of the amorphous GST film which can improve the long term stability of the meta-stable amorphous phase. @FootnoteText@ @footnote 1@S. Hudgens and B. Johnson, Mater. Res. Soc. Bull. November, 2002, p.829. @footnote 2@S. Lai, Tech. Dig. Int. Electron. Devices Meet. Washington, DC, 2003, p.255. @footnote 3@S.Y. Lee and K. Kim, Int. Conference on Integrated Circuit Design and Technology, 2004, p.45. @footnote 4@Y. N. Hwang, S. H. Lee, S.J. Ahn, S.Y. Lee, K.C. Ryoo, H.S. Hong, H.C. Koo, F. Yeung, J.H. Oh, H.J. Kim, W.C. Jeong, J.H. Park, H. Horri, Y.H. Ha, J.H. Yi, G.H. Koh, G.T. Jeong, H.S. Jeong and K. KiM, Tech. Dig. Int. Electron. Devices Meet. Washington, DC, 2003, p.893 .

Plasma Science and Technology
Room 2011 - Session PS2-ThA

Plasma Modeling

Moderator: T. Yagisawa, Keio University, Japan

2:00pm **PS2-ThA1 A Generic Framework of Surface Kinetics Modeling for Plasma-Surface Interactions*, H.H. Sawin,*** *B. Bai,* Massachusetts Institute of Technology **INVITED**

A generic surface kinetics model was developed to model the plasma surface kinetics of both etching and deposition processes. The model is based on the translation of a mixed-layer at the substrate surface during plasma processing that is mixed by ion bombardment. This layer translates into the substrate when more material is removed than deposited (etching) and away from the substrate when the net flux is positive. The kinetics of the etching and deposition are based on the assumption that the surface is well mixed by ion bombardment; therefore, the number of any given moiety can be computed based on the elemental composition of the layer. In addition, vacancy species within this layer are also computed. Ion induced etching and sputter removal of surface species are then readily modeled based upon the moiety concentrations. Incorporation of neutrals is based on the concentration of the dangling bonds, as calculated from vacancy species. All major etching characteristics can be explained using this generic modeling approach, including the dependence of the etching yield on the neutral to ion flux ratio, on the neutral composition, on the ion composition, on the ion energy, and on the ion incident angle. The etching processes of silicon in chlorine and bromine plasmas were used as examples and good agreement between experimental results and model prediction were observed. This modeling approach is extremely fast in development and application while capturing all major etching behaviors. Furthermore, the kinetic coefficients determined by this model are readily converted into the probabilities needed for dynamic Monte Carlo 3-D profile simulators.

2:40pm **PS2-ThA3 Modeling of Roughness Evolution and Instability during Si Plasma Etching***, P. Angelikopoulos, V. Constantoudis, G. Kokkoris, G. Mpoulousis, P. Xidi,* ***E. Gogolides,*** Institute of Microelectronics, NCSR "Demokritos", Greece

As the dimensions of fabricated features go down to nanometer scale, the roughness of their surfaces affects increasingly their physicochemical behavior and may degrade electrical, optical or other device performance. Thus, the control and understanding of roughness formation during plasma etching is of primary importance in micro- and nano-patterning technology. A common finding of past works devoted to the experimental and theoretical investigation of roughness origins and formation on plasma etched Si surfaces was the instability observed in the roughness evolution, i.e. the root mean square (rms) of surface roughness increases linearly with time. A possible explanation for the roughness instability was based@footnote 1@ on the reemission of etchant species (sticking probability 0 for first impact 1 for the second). In this work, simulation of Si surface etching at the nano-scale is done by Monte Carlo and/or continuum models. An alternative mechanism for the roughness instability is formulated, which considers the effect of reactive neutral species, ions and etching resistant species; the latter may come from the sputtering of electrode and/or reactor-wall material or from non-volatile plasma species. These etching resistant particles contribute to roughness formation by inducing local nano-masking. Preliminary simulation results suggest a sufficient reproduction of experimental trends in roughness behavior of Si surfaces etched by SF@sub 6@ plasma.@footnote 2@ AFM images are characterized and compared to the simulation results. @FootnoteText@ @footnote 1@ Y.-P. Zhao, J. T. Drotar, G. C. Wang, and T. M. Lu, Phys. Rev. Lett. 82, 4882 (1999).@footnote 2@ E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, and V. Constantoudis, Microelectron. Eng. 73-74, 312 (2004). .

3:00pm **PS2-ThA4 C@sub 4@F@sub 6@/Ar Plasma Modeling by using Feature Simulation and Elementary Reaction Analysis***, **Y. Shimogaki**, H. Watanabe,* The University of Tokyo, Japan*; Y. Egashira,* Osaka University, Japan*; S.-Y. Kang, I. Sawada,* Tokyo Electron Limited, Japan

C@sub 4@F@sub 6@ is an attractive fluoro-carbon gas to replace commonly used C@sub 4@F@sub 8@, because of the much lower global warming potential (GWP) compared to C@sub 4@F@sub 8@. We have examined the deposition kinetics of a-C:F film from C@sub 4@F@sub 6@ plasma in a CCP reactor, assuming that the reactor is a completely stirred tank reactor (CSTR). The residence time dependency of deposition rate and chemical species analysis using appearance mass spectroscopy (AMS) revealed that main deposition species may be an activated C@sub 4@F@sub 6@. Elementary reaction analysis also confirms this reaction model. Feature profile simulation on the deposition profile within an over-hang test structure suggests that ionic species are contributing to initiate deposition reactions.

3:20pm **PS2-ThA5 Dry Process under Competition Among Charging, Etching, and Deposition***, **T. Makabe**, T. Shimada, T. Yagisawa,* Keio University, Japan

Dry etching is a highly selective technique for functions of positive ions, electrons, neutral radicals, and photons produced by low temperature plasmas. In particular, dielectric etching is a competitive process among charging, etching and deposition at each of local positions of a geometrical structure exposed to reactive plasmas. Even on a dielectric surface, a wall may have a finite conductivity under photo irradiation from plasmas. Plasma etching is adjacent to the damage, such as charging, thermal, irradiation, caused by these elements. In this work we have performed the feature profile simulation of a trench on SiO@sub 2@ and organic low-k by considering the competition among charging, etching and deposition. The effective etch-yield of SiO@sub 2@ exposed to fluorocarbon plasmas is available from a beam experiment and etch rate observation. The sheath area adjacent to the patterned surface is, in principle, subject to distortion by the local charging in the inside of the trench. Undisturbed radial plane from the surface is automatically prepared. A time-averaged 2D plasma structure in a two-frequency CCP reactor of several cm in dimension is connected to the wafer surface having a pattern of a size of sub-micron. The influence of the charging and/or deposition on the etching of SiO@sub 2@ and organic low-k is numerically discussed in term of the feature profile evolution. Also the effect of the surface conductivity on the feature profile is investigated.

3:40pm **PS2-ThA6 Edge Effects in Reactive Ion Etching: The Wafer- Focus Ring Gap****, **N.Y. Babaeva**, M.J. Kushner,* Iowa State University

The termination of the edge of the wafer in reactive ion etching is important to obtaining uniform reactants (composition, magnitude and energy) across the entire substrate. The use of focus rings is designed to maintain a seamless transition of reactants across the edge of the wafer. Non-optimum termination may result in a larger than desired edge exclusion where useful product cannot be obtained. There is an unavoidable gap between the edge of the wafer and terminating structures, such as focus rings. The issue we have investigated is how influential the wafer-focus ring gap is in affecting the uniformity of reactants across and to the edge of the wafer and in affecting the ion flux into the gap. The latter is important in that the ion flux may be incident on the side edge or the bottom of the wafer in the case of beveled edges. This investigation was performed with a fluid model having an unstructured mesh that enables resolution of a large dynamic range in spatial scales and arbitrary shapes. The modeling platform, nonPDPSIM, was improved by incorporating ion momentum equations and ion drag on neutrals. Results will be presented for RIE plasmas sustained in Ar, Ar/Cl@sub 2@ and Ar/fluorocarbon systems at tens of mTorr. The width and depth of the wafer-focus ring gap was varied for different powers and frequencies. @FootnoteText@ *Work supported by Semiconductor Research Corp. and the National Science Foundation.

4:00pm **PS2-ThA7 Development of High Aspect Ratio, Selective Si Etch Model in CCP Halogen Plasma***, D. Fischer, W. Jacobs, A. Kersch, **W. Sabisch**,* Qimonda AG, Munich, Germany*; S. Barth, A. Henke,* Qimonda AG, Dresden, Germany*; J. Sobe,* Qimonda AG, Munich, Germany*; A. Steinbach,* Qimonda AG, Dresden, Germany*; S. Wege,* Qimonda AG, Munich, Germany*; M. Reinicke,* Dresden University of Technology, Germany

Silicon etching based on a HBr/O@sub 2@/NF@sub 3@ plasma generated in a dual frequency 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 the development of an electrical CCP chamber model as well as a Si etch rate model for high aspect ratio etch selective to an oxide mask. The CCP chamber model is an equivalence circuit model comprising match, chamber impedance from stray capacity and chuck resistivity, plasma sheath and plasma bulk with a resistivity model for electronegative plasma. The parameter values are consistent with a large amount of tool data. The result of the model is a consistent set of electron density, ion current and VDC values for different electronegativities as a function of the tool parameter. In a second step a large set of planar Si and SiO@sub 2@ etch rate data is evaluated with the plasma values to calibrate a plasma and surface reaction model. The selective Si/SiO@sub 2@ etch model is finally combined with an ion- and neutral particle transport model in the trench structure@footnote 1@ to provide etch depths depending on process conditions.@footnote 2@The results of the model are in good agreement with a large amount of data ranging from tool data to trench etch data. @FootnoteText@ @footnote 1@ W. Jacobs et al, IEDM Tech. Digest, Session 35/5, 2002@footnote 2@ A. Kersch et al., AVS 2004, PS2-MoM3.

4:20pm **PS2-ThA8 Global Model of a Dual Frequency Capacitive Discharge***, **P. Levif**, P. Chabert,* Ecole Polytechnique, France*; M.M. Turner,* Dublin City University, Ireland

The physics of capacitive discharges has recently been reinvigorated with the rise of interest in multiple-frequency excitation and the related need to widen the range of frequencies that are used. A major attraction of dual-frequency excitation is that it promises independent control of the ion flux and the ion energy, which is not the case in single frequency excitation. The electron heating mechanisms occurring within the dual-frequency sheath region were recently investigated by Turner and Chabert (Submitted to Physical Review Letters). It was shown that the heating (either collisional or collisionless) produced by the superposition of the two frequencies is much larger than the sum of the two frequency contributions. In the present paper, we use the heating models developed to construct a global model of a dual-frequency capacitive discharge operated in argon. For this, we must also discuss the dynamics of the sheath, s(t), to obtain the equivalent of a dual-frequency Child law which relates the applied rf voltage, the electron density and the sheath size. By coupling the power and particle balance to the Child law mentioned above, one can obtain a self-consistent solution for all the plasma parameters. As an example, for a discharge excited by the combination of 13 and 143 MHz, the electron density increases by a factor 15 when the ratio of the high-frequency current to the low-frequency current amplitude increase from zero (i.e. the single 13 MHz case) to six.

4:40pm **PS2-ThA9 Particle-in-Cell Simulation of Beam Extraction Through Grid Holes with Application to Neutral Beam Sources***, **S.K. Nam**, D.J. Economou, V.M. Donnelly,* University of Houston

A particle-in-cell (PIC) simulation of beam extraction through a grid hole in contact with plasma was developed. Particular emphasis was placed on plasma molding over the hole, ion neutralization (by wall collision) in high aspect ratio holes, and the energy and angular distributions of the residual ions and fast neutrals in the beam downstream of the hole. The target application was the generation of neutral beams for future charge-free microelectronics manufacturing. Neutral beam processing requires collimated beams with controlled energy. The ion energy-angular distributions (IEAD), for ions striking the sidewall of the hole, indicated that ions with lower energy tend to be affected more by plasma molding, resulting in larger incident angles on the sidewall. The energy and angular distributions of ions and fast neutrals at different locations along the hole surface showed that ions which neutralize on the top section of the surface of the hole are bad, in the sense that these ions yield divergent neutral beams of relatively low energy. Ions that neutralize along the bottom section of the surface of the hole are good ions, in the sense that these ions yield neutral beams that are less divergent and retain more of the energy of the parent ions. This finding prompted the development of strategies to maximize the fraction of good ions.

Plasma Science and Technology
Room 3rd Floor Lobby - Session PS-ThP

High Pressure Discharges and Novel Diagnostics & Sources Poster Session

PS-ThP2 Numerical Analysis of Oxygen Positive Column in Atmospheric Pressure Glow Discharge Plasmas*, **Y. Ichikawa**, T. Suzawa, M. Narita,* Fuji Electric Device Technology, Japan

Recently, atmospheric pressure (AP) glow discharge plasmas have been studied by a number of researchers, because many applications are expected. The properties of AP plasmas, however, have not been understood very well yet. Thus, we have made an attempt to extend a positive column theory based on the ambipolar diffusion model to the AP range. Oxygen discharges have been widely used to various applications such as surface treatment for removal of organic materials, ashing, and ozonizing. For this reason, it is interesting to analysis oxygen AP positive column plasmas. Thus we carried out a numerical analysis of this discharge. In the simulation, we took into account four neutral species, O, O@sub 2@, O@sub 3@ and O@sub 2@(a@super 1@@DELTA@@sub g@), and eight ion species, O@super +@, O@sub 2@@super +@, O@sub 3@@super +@,O@sub 4@@super +@, O@super -@, O@sub 2@@super -@, O@sub 3@@super -@ and O@sub 4@@super -@. The transport equations for these charged and neutral species were solved simultaneously, and obtained the electron temperature and the abundance ratio of species self-consistently. The obtained results showed that the behavior of the plasma at the atmospheric pressure is quite different from that of the medium gas pressure range. The plasma density is higher than the electron density by more than an order of magnitude at higher gas pressures, and the major negative species is O@sub 3@@super -@ at the atmospheric pressure. For the positive ions, O@sub 4@@super +@ becomes the majority ion at around the atmospheric pressure. The obtained composition of neutral species showed that O@sub 3@ increases as the tube radius decreases at the atmospheric pressure.

PS-ThP3 A New Production Method of Negative-Ion-Plasma in an Extremely High Dielectric-Constant Discharge Tube*, **K. Kusaba**,* Tokai University, Japan*; Y. Ikeda,* KYOCERA Co. LTD., Japan*; K. Shinohara,* Japan High Frequency Co., LTD*; H. Shindo,* Tokai University, Japan

Negative ions in plasmas are much attractive species in material processing, such as ion implantation, CVD and etching in ULSI fabrications. The objective of this work is to study a new negative ion plasma source. In particular, an innovative method to produce a high density negative ion plasmas is proposed by employing RF surface-wave plasma with a extremely high dielectric constant discharge tube. In this work, a negative ion plasma is produced by employing the after-glow appeared in the resonance density of the surface-wave which is enhanced by a extremely high dielectric constant discharge tube. The surface-wave plasmas of O2 and SF6 were produced in a discharge tube by supplying 13.56 and 60 MHz power. The two discharge tubes of a ceramic of TiCa-TiMg, K-140, which is commercially available from KYOCERA Co. and quartz are employed, and their permittivities are, respectively, 140 and 3.8. The optical emission line measurements were carried out from the lateral view. The axial decay rate of the intensities of the optical emission lines FI in SF6 plasma were 5 times faster in the K-140 discharge tube than in the quartz. In particular, a sudden precipitation of the line intensity could be observed, and this is due to the surface-wave ending at the resonance density, providing a high density after-glow. In O2 plasma, in this after-glow region, the OI emission lines of 777 and 845 nm, which are originated from the mutual neutralization of O- and O+, were observed to be very much enhanced after the sudden precipitation, indicating the rich negative ions populated in this region. Furthermore, the emission line of OI 645 nm, which is known free from the mutual neutralization, was not observed in the after-glow. This fact clearly demonstrates that the line intensity enhancement in the downstream is due to the negative oxygen ion. While in the quartz discharge tube the line intensity decayed just simply and monotonically.

PS-ThP4 Spectroscopic Study of Fluorocarbon Plasma Gas Phase Chemistries in High Density Plasma for a Submicron Contact Hole Etching*, **G.H. Kim**,* ETRI, Korea*; K.T. Kim, C.I. Kim,* Chung-Ang University, Korea*; S.G. Kim,* ETRI, Korea*; J.G. Koo,* ETRI*; T.M. Roh, J.D. Kim,* ETRI, Korea

As ultra large scale integrated (ULSI) devices are scaled down, highly selective SiO@sub 2@ etching and submicron contact hole etching process are increasingly required. Silicon nitride is used as a passivation layer that protects circuits from mechanical and chemical attack, or as an etch stop layer, enabling the fabrication of certain damascene and self-aligned contact (SAC) structures. Previous studies focused on either anisotropic etching or selective etching of SiO@sub 2@ over Si@sub 3@N@sub 4@ or Si using conventional low density plasma sources. Recently, high density plasma (HDP) single wafer etching tools have attracted a lot of attention, mainly because HDP sources operate at low pressure and allow independent control of ion flux and ion energy. Consequently, the plasma-surface interactions become significant, and surface conditions such as the temperature and cleanliness of the reactor wall play an important role determining both the gas phase chemistries and the surface reactions deposition and etching on the wafer surface. In this study, we present a highly selective SiO@sub 2@ etching and submicron contact hole etching with a hydro-fluorocarbon gas (CHF@sub 3@ and CH@sub 2@F@sub 2@) in addition to CF@sub 4@ and C@sub 4@F@sub 8@ plasma chemistry in high density plasma and discuss the important species required for protecting the nitride surface and controlling the polymer inhibitor by using optical emission spectroscopy and X-ray photoelectron spectroscopy.

PS-ThP5 Electron Density and Electron Temperature of Narrow-Gap RF Plasma Polymerization System Measured by Highly-Sensitive Double Surface Wave Probe Technique*, **K. Kinoshita**,* MIRAI-ASET, Japan*; K. Nakamura, O. Hirano,* Chubu University, Japan*; Y. Hyodo,* MIRAI-ASET, Japan*; O. Kiso,* MIRAI-ASRC, AIST, Japan*; J. Kawahara,* MIRAI-ASET, Japan*; Y. Hayashi,* NEC, Japan*; S. Saito,* Selete, Japan*; H. Sugai,* Nagoya University, Japan*; T. Kikkawa,* Hiroshima University, Japan

A plasma copolymerization technique has been developed to achieve scalability of low-k materials for two or three technology nodes of ULSIs. In-situ QMS analysis showed that multistep dissociation of the precursor monomers progressed in the plasma.@footnote 1@ Low-k property of the deposited film was lost by over dissociation. Thus, the following three points are indispensable; (a)reduction of electron density (Ne), (b)lowering electron temperature (Te), and (c)reduction of gas residence time. In this study, electron temperature was measured for actual deposition plasma by double surface wave probe technique. This technique enables to measure Ne and Te by the difference of surface wave resonance frequencies.@footnote 2@ An RF plasma CVD system for 300 mm wafer was used. A cyclosiloxane monomer with six-member ring and organic functional groups was used as a precursor monomer with helium carrier gas.@footnote 3@ While increasing precursor flow rate from 0 sccm to 10 sccm (1.7 %), Ne decreased rapidly from 5.2E10 cm@super -3@ to 1.4E10 cm@super -3@. On the other hand, Te decreased gradually from 2 eV to 0.5 eV at the flow rate from 0 sccm to 40 sccm (6.7 %), and kept constant over this flow rate range up to 100 sccm. These results indicate that Te of the plasma polymerization process was low enough even in the helium discharge. Radial distributions of Ne and Te were affected by the gas pressure change. Uniform discharge was obtained at the gas pressure of 400 Pa, and the source power of 200 W (Ne=1.5E10 cm@super -3@). To optimize plasma polymerization process, some hardware knob for uniformity control would be effective to achieve better process margins. This work was supported by NEDO. @FootnoteText@ @footnote 1@ K. Kinoshita, et al., Proc. Dry Process Symp. 2003, Tokyo, 3-1, 61 (2003).@footnote 2@ O. Hirano, et al., Abst. Spring Meeting Jpn. Soc. Appl. Phys., 25a-W-7, (2006)@footnote 3@ Y. Hayashi, et al., Proc. 2004 IEEE Int. Interconnect Technol. Conf., 12.3, (2004).

PS-ThP6 Predicting Ion Energy Distribution Function for Multi-Frequency Capacitive Discharges*, **A. Wu**, M.A. Lieberman, J.P. Verboncoeur, A.J. Lichtenberg,* University of California, Berkeley

In single and multiple frequency capacitive discharges used for semiconductor processing, the ion energy distribution function (IEDF) is important for determining the effects of ions at the wafer. The ability to predict the IEDF from the applied discharge voltages is greatly desired. We present particle-in-cell simulations for different frequencies and voltages to determine the IEDF, and we develop a theoretical model to predict the IEDF for any number of frequency drives, as long as the voltage across the sheath is known. In the model, we use a frequency filtered version of the voltage applied to the wafer to determine the ion response function. The filter function shape depends mainly on the ratio of the ion transit time across the sheath to the various applied frequencies, and is implemented in the model using Fourier transform techniques. We are exploring the use of a filter function given by Benoit-Cattin (1968)@footnote 1@ to determine the ion response, in order to predict the IEDF. A further refinement can be used for the regime where the driving frequency is approximately the same as the ion transit time. @FootnoteText@@footnote 1@P. Benoit-Cattin and L. C. Bernard, "Anomalies of the Energy of Positive Ions Extracted from

High-Frequency Ion Sources. A Theoretical Study," J. Appl. Phys. 39, 5723 (1968).

PS-ThP7 A Transmission Line Microwave Interferometer for Monitoring of Electron Density in Plasma Processing Tools*, **C.H. Chang**, J.Y. Jeng, C. Lin, K.C. Leou,* National Tsing Hua University, ROC

We developed a transmission line microwave interferometer for monitoring of electron density for applications in process real-time feedback control of plasma based semiconductor fabrication tools, such plasma etchers or PECVDs. The sensor was a dielectric transmission-line where microwave propagates at a phase velocity determined by the structure and the electron density of the surrounding plasma. 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 2.4 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 6 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.

PS-ThP8 Floating Probe for Electron Temperature and Ion Density Measurement Applicable to Processing Plasmas*, **C.W. Chung**,* Hanyang University, South Korea

A floating type probe(FP) and its driving circuit using the nonlinear characteristics of the probe sheath was developed and the electron temperature and the plasma density which is found from ion part of the probe characteristic(ion density) were measured in inductively coupled plasmas(ICP). The FP was compared with a single Langmuir probe and it turned out that the FP agrees closely with the single probe at various rf powers and pressures. The ion density and electron temperature by the FP were measured with a film on the probe tip coated in CF@super 4@ plasma. It is found that the ion density and electron temperature by the FP were almost the same regardless of the coating on the probe tip while a single Langmuir probe does not work. Because the floating type probe is hardly affected by the deposition on the probe tip, it is expected to be applied to plasma diagnostics for plasma processing such as deposition or etching.

PS-ThP9 EEPF Measurement in SF6/O2 and CF4/O2 Gas Mixture Capacitively Coupled Plasma*, **S.K. Ahn**, S.J. You, H.-Y. Chang,* Korea Advanced Institute of Science and Technology, Republic of Korea

We have been measured the plasma parameters and EEPF (Electron Energy Probability Function) in a capacitive discharge with some mixtures of processing gases, such as SF6/O2 and CF4/O2. The measurements were achieved at various gas mixing ratios under constant discharge current and pressure conditions. Through the experiment, we have found that as the mixing ratio of SF6 increase, the effective electron temperature increases, while the electron density decreases. And in case of CF4 mixing, the variation trend of the effective electron temperature and the electron density is very similar to that of SF6 mixing case. Thus, it apparently looks like mixing SF6 or mixing CF4 in O2 discharge affect the plasma parameters with similar discharge physics. However in our EEPF measurement, it has been found that mixing SF6 and mixing CF4 in O2 discharge influence the plasma with quite different manners. The low energy part of EEPF is depleted in both case of increasing SF6 mixing ratio and increasing CF4 mixing ratio. But the high energy electron population in EEPF only depends on SF6 mixing ratio. That is, the high energy electron population in EEPF is enhanced with increasing SF6 mixing ratio, while almost independent of CF4 mixing ratio. These gas mixing effects can be analyzed by considering elastic collision and vibrational excitation collision between electrons and the fluoride gases.

PS-ThP10 Optical Emission Measurements of Dual Frequency Capacitively Coupled Plasmas*, **E.C. Benck**, K.L. Steffens,* National Institute of Standards and Technology

Dual frequency capacitively coupled plasma sources are becoming increasingly important in semiconductor manufacturing processes. An imaging spectrometer combined with a high speed intensified CCD camera was used to obtain spatially and temporally resolved measurements of the optical emission from dual frequency (2 MHz & 13.56 MHz or 2 MHz & 27.12 MHz) plasmas created in a Gaseous Electronics Conference (GEC) reference reactor. The vertical distribution of the argon 750.4 nm transition was measured at the center of the discharge. Significant changes in the temporal and vertical optical emission distributions were observed with changing feed gas (Ar, CF@sub 4@, and O@sub 2@) and gas pressure (100 mT to 1000 mT). The temporal distributions were insensitive to the amplitude of the lower frequency voltage. Changing from a single powered electrode to two separate powered electrodes also had a significant impact on the time resolved optical emission.

PS-ThP11 Anisotropic Deposition of Cu with a Plasma CVD Reactor Equipped with a High Power ICP H Source*, M. Shiratani, J. Umetsu, **S. Iwashita**, K. Koga,* Kyushu University, Japan

We have realized anisotropic deposition of Cu, for which Cu is filled preferentially from bottom of trenches without being deposited on their sidewall, by H-assisted plasma CVD.@footnote 1,2@ Such type of deposition has a potential to overcome common problems associated with conformal filling: namely, small crystal grain size below half of the trench width, and formation of a seam with residual impurities of relatively high concentration. A high flux of H atoms is required to deposit high purity Cu films at a high rate, because H irradiation to Cu films is effective in reducing impurities in the films. For this purpose, we have increased the maximum discharge power P@sub H@ of the ICP H source from 150 W to 1000 W. To obtain information about the H flux, we have examined dependence of optical emission intensity of H@alpha@(656 nm) on P@sub H@ as a parameter of a gas flow rate ratio R=H@sub 2@/(H@sub 2@+Ar). The following results are obtained in this study. 1) H@alpha@ intensity increases with P@sub H@. 2) H@alpha@ intensity is 10-100 times as high as that for our previous H source. 3) We have filled trenches completely with high purity Cu at a rate above several nm/min for R=11% using anisotropic deposition. Moreover deposition stops automatically just after filling trenches completely. @FootnoteText@ @footnote 1@K. Takenaka, et al., Pure. Appl. Chem. 77(2005)391.@footnote 2@K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) 1903. .

PS-ThP12 Characteristics of Inductively Coupled Plasma Using Internal Multiple U-type Antenna for Ultra Large-area FPD Processing*, **J.H. Lim**, K.N. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea

Inductively coupled plasmas (ICP) have been investigated for the processing of various materials as one of the high density (1011~1012 cm@super -3@) and low gas pressure plasma sources. But this ICP source have some problems in the processing of large-area, due to the cost and thickness of its dielectric material and the large impedance of the antenna when scaling up to large areas. However, by inserting an antenna into the plasma, more production applicable large-area ICP is feasible due to the induction of a strong electric field in the plasma and the efficient power transmission to the plasma. In this work, an internal-type antenna (multiple U-type antenna) was used as a large-area (2,300 mm x 2000 mm) inductively coupled plasma (ICP) source. Characteristics of the plasma were measured using a Langmuir probe located on the sidewall of the chamber and the use of the multiple U-type antenna showed higher plasma density. Electrical properties of multiple U-type antenna were measured by impedance analyzer. By changing the antenna arrangement and distance of antenna array, the uniformity of the plasma has changed significantly. By optimizing the antenna arrangement, the plasma uniformity less than 10% could be also obtained within the substrate area.

PS-ThP14 New Method for Measurement of Electron Temperature using Wave Cutoff Frequency and Wave Absorption Frequency in Plasmas*, **J.H. Kim**,* Korea Research Institute of Standards and Science, Korea*; D.-J. Seong, Y.H. Shin,* Korea Research Institute of Standards and Science

Wave absorption probe@footnote 1@ and wave cutoff probe@footnote 2@ were developed for the measurement of electron density. The wave absorption probe relies on the resonant absorption of surface waves excited in a cavity at the antenna head. A network analyzer feeds a microwave to the antenna and displays the frequency dependence of power absorption by measuring reflected power. The wave absorption frequency can give the electron density when the electron temperature is

known. For measuring the cutoff frequency, a microwave is introduced through the radiating antenna to the plasma and the transmitted wave is detected on the other antenna connected to the receiving port of network analyzer. The wave cutoff frequency can directly give the electron density. Therefore, we can measure both of the absorption frequency and the cutoff frequency with one cutoff probe system. In dispersion relation of surface wave, the absorption frequency is related with the electron density and the electron temperature. Therefore, we can deduce the electron temperature using the absorption frequency and the electron density measured by the cutoff frequency. The measured electron temperature is compared with those got by using a Langmuir probe. @FootnoteText@ @footnote 1@ K. Nakamura et al., J. Vac. Sci. Technol.A 21, 325 (2003)@footnote 2@ J. H. Kim et al., Review of Scientific Instruments Vol. 75, 2706 (2004) .

PS-ThP15 Measurements of Cu Densities at the Ground and Metastable States in a Magnetron Sputtering Plasma Source with a Cu Target*, K. Sasaki*, *J.-S. Gao, N. Nafarizal, H. Toyoda, S. Iwata, T. Kato, S. Tsunashima, H. Sugai,* Nagoya University, Japan

In the cases of light elements and rare gases, the densities of metastable states are negligible in comparison with the densities of the ground states. On the other hand, in the cases of metal atoms, the densities of metastable states are possibly much higher because of the low excitation energies. The excitation energy of the metastable @super 2@D state of Cu is 1.39 eV, which is lower than electron temperatures of usual magnetron sputtering plasmas. In this case, the density of the metastable state could be comparable to the ground-state (@super 2@S state) density. In this work, we measured the spatial distributions of the Cu atom densities at the ground and metastable states in a conventional magnetron sputtering plasma source with a Cu target by laser-induced fluorescence imaging spectroscopy. The absolute densities of the ground and metastable states were determined by ultraviolet absorption spectroscopy employing a Cu hollow cathode lamp as the light source. As s result, it was found that the density of the metastable state was on the same order as the ground-state density. The spatial distributions of the ground and metastable densities were different. Accordingly, the metastable density affects the total Cu atom density and the distribution. In addition, since the chemical reactivity of the metastable state may be different from that of the ground state, it is necessary to consider the influence of the metastable state in the kinetics of Cu in the gas phase and on the surface. @FootnoteText@ This work was supported by 21st century COE (Center of Excellence) Program "Information Nano-Devices Based on Advanced Plasma Science" of Nagoya University.

Plasma Science and Technology
Room 2009 - Session PS1-FrM
Plasma-Surface Interactions III

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

8:00am **PS1-FrM1 Subplantation and Interface Modification during Ion Assisted Low-Pressure Plasma Deposition of Oxides at the RF-Biased Electrode**, *A. Amassian,* Cornell University*; P. Desjardins,* ***L. Martinu,*** Ecole Polytechnique de Montreal, Canada

Significant research effort has been devoted to linking plasma characteristics, ion-surface interactions, and film properties in PVD, PECVD, and hybrid PECVD/PVD processes, leading to a qualitative understanding of surface processes and thin film growth mechanisms. In this paper, we report on the sub-surface effects of subplantation in an O@sub 2@ RF discharge during plasma treatment and thin film deposition at the RF-biased electrode. Using in situ real-time spectroscopic ellipsometry (RTSE), we have obtained time-resolved quantitative information about depth-dependent modifications of c-Si(001) exposed to intense ion bombardment under conditions typically used for oxide deposition. RTSE analysis indicates almost immediate damage formation (1 to 2s); it forms near the surface of the target on top of an O deficient interfacial damage layer (DL). Both layers experience a self-limiting growth behavior, as oxide and DL thicknesses reach bias-dependent saturation values, determined by the maximum ion penetration depth. The results are independently confirmed by cross-sectional high resolution TEM analysis. The in situ experimental study was complemented by Monte-Carlo TRIDYN simulations based on the binary collision approximation, which were modified to calculate dynamic changes in the structure and composition of a target exposed to a broad-energy ion source (ion energy distribution at RF electrode) at high fluence. This novel approach has allowed us to obtain the first quantitatively accurate simulation results of ion bombardment-induced sub-surface oxygen incorporation on time-scales from <

8:20am **PS1-FrM2 Process Performance of H@sub 2@ Remote Plasma Based Photoresist Ashing Processes and Their Influence on ULK Materials Modifications**, ***M.S. Kuo,*** *G.S. Gottlieb,* University of Maryland at College Park*; P. Jiang,* Texas Instruments*; P. Lazzeri, M. Bersani, S. Pederzoli, M. Anderle,* ITC-irst, Center for Scientific and Technological Research, Italy

We have examined the damage introduced in a blanket ultralow-k (ULK) dielectric material (nanoporous silica - NPS) and compared it with that inflicted on a low-k (LK) material (chemical-vapor-deposited organosilicate glass - OSG) for remote plasma conditions used to ash 193 nm photoresist (PR). For different substrate temperatures and H@sub 2@-based ashing chemistries, we found little damage in ULK/LK materials for H@sub 2@-based ashing processes without N@sub 2@. The damage depth increased dramatically with N@sub 2@ addition to H@sub 2@, while the PR ashing rate did not increase with N@sub 2@ addition. For our remote plasma, elevated substrate temperature (200 to 275 °C) conditions, N@sub 2@ addition to H@sub 2@ is ineffective in reducing ULK damage relative to (PR) ashing rate. The higher activation energy of PR ashing (~0.4 eV) than that of ULK/LK damage introduction (~0.1 eV) for remote plasma processing favors a higher substrate temperature for ashing process optimization. In addition, to address issues connected with sequential plasma etching and ashing steps, we also investigated the effect of surface residues due to prior capacitively coupled plasma (CCP) etching on PR ashing process efficacy and ULK/LK damage. The application of these approaches to etching/ashing actual trench structures is also described. Finally, we used D@sub 2@ ashing processes to investigate the behavior of deuterium/hydrogen in ULK/LK materials.

8:40am **PS1-FrM3 Measurement of Etching Kinetics and Surface Roughening of SiO2 and Coral Films during Plasma Etching**, ***Y. Yin,*** *H.H. Sawin,* Massachusetts Institute of Technology

Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. The primary cause of sidewall roughening is the templating of mask roughness into the underlying film. Specifically, the inherent roughening of photoresist provides the mask for templating effect. To fully understand the sidewall roughness evolution, it is critical to understand the mechanism of the inherent roughening of photoresist as well as other materials, such as low-k dielectric film. The etching kinetics and surface roughening of thermal SiO2 and low-k dielectric Coral in Ar, C2F6/Ar, and C4F8/Ar plasma beams have been measured as a function of ion energy, ion bombardment angle, etching time and plasma composition in an inductively coupled plasma beam system. For all plasma chemistries, the etching yield at normal impingement angle scales linearly with the square root of ion energy. The angular dependence of the etching yield of both films in Ar plasma followed the typical sputtering yield curve, with a maximum around 60-75 degree off-normal angle. By adjusting the plasma etching conditions, the etching yield in fluorocarbon plasmas can follow either the ion-enhanced-etching yield curve or a sputtering-like yield curve. The surface roughening of both films showed different trends in Ar and fluorocarbon plasmas. In Ar plasma, both films stayed smooth after etching at normal angle while became rougher at grazing angles. Specifically, the striation formed at grazing angles can be either parallel or transverse to the beam impingement direction. More interestingly, the sputtering caused roughening at different off-normal angles can be qualitatively explained combining the corresponding angular dependent etching yield curve. In fluorocarbon plasmas, the films kept smooth at normal angle; while at grazing angles, the surface can be either rougher when the etching is sputtering-like or remain smooth when ion-enhanced etching is dominant.

9:00am **PS1-FrM4 Spectroscopic Studies of Ammonia Plasmas**, ***S.J. Kang,*** *V.M. Donnelly,* University of Houston

Surprisingly, there is little understanding of the basic chemical mechanisms in PE-CVD of carbon-containing materials such as carbon nanotubes, including the role of added NH@sub 3@. In this study we investigate the plasma chemistry of NH@sub 3@ decomposition in NH@sub 3@/Ar-containing plasmas at 1 Torr. Absolute NH@sub 3@ number densities were measured as a function of inductively-coupled plasma power and substrate temperature (T@sub s@) by ultraviolet (UV) absorption spectroscopy. Plasma-induced optical emission was used to qualitatively identify species such as NH and H, formed from NH@sub 3@ electron impact dissociation and subsequent reactions. A new "self-actinometry" method was introduced to measure the absolute number density of N@sub 2@ that is formed following dissociation of NH@sub 3@ and secondary reactions. In this approach, small amounts of N@sub 2@ were added to the NH@sub 3@-containing plasma, leading to an increase in the N@sub 2@ C->B state emission intensity, above the level of intensity observed in the absence of added N@sub 2@. By extrapolating to zero added N@sub 2@, we obtain the calibration factor that allows us to convert relative N@sub 2@ C-> B emission intensities into absolute number densities. We assume that very little of the added N@sub 2@ is dissociated; given its strong bond energy and low T@sub e@ at 1 Torr, this assumption is valid. The number densities of NH@sub 3@ decreased with increasing power and T@sub s@, reaching >90% dissociated at 400W and 900K. Conversely N@sub 2@ densities increased with power and T@sub s@. It appears that the majority of dissociated NH@sub 3@ leads to the formation of N@sub 2@ (i.e. the total nitrogen content is conserved in the sum of these two species).

9:20am **PS1-FrM5 Study of Downstream NH@sub 3@ Plasma Damage to Low k Dielectrics**, ***J. Bao,*** *H. Shi, J. Liu, P.S. Ho,* The University of Texas at Austin

Carbon Doped Oxide (CDO) films were treated by downstream NH@sub 3@ plasma. The effects of film porosity, ion energy, process time, substrate temperature on carbon depletion and nitrogen incorporation were studied by In-situ angle resolved X-ray photoelectron spectroscopy. Transmission electron microscopy, Fourier transform infrared spectroscopy, Spectroscopic ellipsometry and Atomic force microscopy were employed to evaluate the extent of damage to the films. NH@sub x@ reacted with the surface weakly bonded groups to form a densification layer. It was observed that this structural modification concentrated mainly within 10 nm at the surface region with the underlying film being undamaged. Mechanism of this plasma damage was investigated by analyzing the residual gas during the process. Hybrid beams damaged low k dielectrics more severely due to the combination of ions and neutrals. Roles of ions and neutrals in the plasma to cause carbon depletion will be compared and discussed. Moisture uptake after the plasma treatment was found to be a major reason to induce dielectric constant increase.

9:40am **PS1-FrM6 Investigation of the Plasma-Activated Catalytic Formation of Ammonia in N@sub 2@ - H@sub 2@ Plasma**, *J.H. van Helden, P.J. van den Oever,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden, D.C. Schram,* ***R. Engeln,*** Eindhoven University of Technology, The Netherlands

In this contribution we report on the investigation of the plasma-activated catalytic formation of ammonia in N@sub 2@-H@sub 2@ containing

plasmas. The formation of ammonia is generally ascribed to stepwise addition reactions from adsorbed nitrogen and hydrogen radicals at the surface, i.e. the ammonia is formed via subsequent hydrogenation of adsorbed nitrogen atoms and the intermediates NH and NH@sub 2@ at the surface. To obtain further insight in the ammonia formation mechanism, the plasma chemistry in a plasma expansion created from mixtures of nitrogen and hydrogen is studied in more detail. The ammonia density and the NH@sub x@ radical density were determined by means of cavity enhanced absorption and cavity ring-down spectroscopy, respectively. It will be shown that ammonia can be formed efficiently in plasmas generated from mixtures of hydrogen and nitrogen. At optimal conditions 11% of the total background pressure, typically in the order of 20 - 100 Pa, was measured to be ammonia. This result turned out to be independent of the position in the plasma reactor. The NH@sub x@ radical densities, however, show a decrease as function from the distance from the exit of the plasma source, i.e. along the expansion axis. The measured NH and NH@sub 2@ densities are at maximum only about 1% of the ammonia density. Also, the NH@sub x@ radicals show the temperature of the plasma expansion, i.e. about 1500 K, while the ammonia molecules show the temperature of the background gas, i.e. about 600 K. These results indicate that the NH@sub x@ radicals are produced in the plasma expansion, while the ammonia is formed at the wall of the reactor. First results of a model describing the trends of the NH@sub x@ radical densities, indicate that NH is mostly produced in reactions of hydrogen molecules with N atoms, while NH@sub 2@ is most probably formed out of NH@sub 3@.

10:00am **PS1-FrM7 Transient Differential Charging of High Aspect Ratio Dielectric Features***, **J.A. Kenney**, G.S. Hwang,* University of Texas at Austin

Plasma processing of high aspect ratio dielectric structures is well-known to encounter complications due to differential charging of features, owing to the dissimilar natures of the ion and electron angular distributions. As device dimensions shrink to below 100 nm, however, the differential charging of the features is no longer an approximate steady-state. Rather, the charging behavior oscillates as individual ions and electrons have a larger impact on the local electric fields. We investigate this phenomenon and its impact on the ion energy and angular distributions exiting the high aspect ratio structure, using a range of values for the surface conduction and entering ion energy and angular distributions. In addition, we look at how this behavior influences feature profile evolution, also as a function of the incoming ion energy and angular distributions.

10:20am **PS1-FrM8 On-wafer Monitoring of Charge Accumulation during Plasma Etching Processes***, **B. Jinnai,*** Tohoku University, Japan*; T. Orita, M. Konishi, J. Hashimoto,* STARC, Japan*; S. Samukawa,* Tohoku University, Japan

The high aspect-ratio (AR) contact hole etching of dielectrics, especially silicon dioxide, is a key process in the manufacture of ULSI devices. During the plasma etching process, a large amount of charge accumulates in the contact hole due to electron shading effect, and leads to many problems, such as charge-build-up damage, etching-stop, and microloading effects. For overcoming these problems, it is indispensable to monitor the amount of charge in the real patterns and control the charge accumulation. In this paper, we evaluated the amount of charging in the real contact holes using our developed on-wafer monitoring sensor. We fabricated more than 100 sensor chips on an 8 inch wafer in a mass production line. The sensor had Poly-Si/SiO@sub 2@/Poly-Si layered structure on silicon substrate and contact holes with two kinds of AR: 10 and 3.3. We measured the potential differences between the top and bottom Poly-Si electrodes during plasma etching processes. It is corresponding to the actual charge accumulation in the contact holes. By increasing AR of contact holes, the potential was drastically enlarged. This result clarified that electron-shading effects were enhanced in higher aspect contact holes and that our developed on-wafer monitoring sensor could achieve in situ monitoring of charge accumulation in the real contact holes.

10:40am **PS1-FrM9 An In-situ Diagnostic to Detect Charging During Plasma Etching***, **E. Ritz**, D. Ruzic,* University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, it is known that defects can occur such as trenching, bowing, and twisting. These defects are particularly noteworthy in the manufacture of DRAM deep-trench capacitors. In order to investigate the role of charging on these phenomena an in-situ diagnostic was fabricated using photolithographic and deposition techniques. The device consists of a base layer of tungsten with alternating layers of silica and tungsten. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The silica layers act as insulators to create discrete measurement layers, provided by the tungsten layers. The tungsten layers are attached to voltage measurement leads and can then be used to measure the build up of sidewall charging at different heights along the via when exposed to a plasma. To determine the effect of geometry, if any, on charging, several aspect ratios were used by maintaining the same device thickness but varying the diameter of the vias. The entire stack is 30 microns thick, with vias ranging in diameter from 30 microns to only 1 micron, thereby producing aspect ratios of 1:1 to 30:1. Results from the diagnostic will be shown for various etching recipes.

11:00am **PS1-FrM10 Reduction of UV Irradiation Damage in CCD Image Sensor using CF@sub 3@I Gas Plasma***, **Y. Ichihashi,*** Tohoku University and Sanyo Electric Co., Ltd., Japan*; Y. Ishikawa,* Tohoku University, Japan*; R. Shimizu, H. Mizuhara, M. Okigawa,* Sanyo Electric Co., Ltd, Japan*; S. Samukawa,* Tohoku University, Japan

The generation of the SiO@sub 2@/Si interface states is one of the most serious problems for the metal-insulator silicon (MIS) devices such as charge-coupled devices (CCDs) or memories. For CCDs, the generation of the interface state causes the increase in dark current. We previously reported that the interface state in MIS devices were increased by the UV irradiation during the plasma process. Especially, the UV wavelength of 200 nm to 350 nm, which induced by C@sub x@F@sub y@ high-molecular-weight radicals, generates the interface states. Namely, the elimination of UV wavelength of 200 nm to 350 nm could keep the low-density interface state even after the etching process. In this paper, we propose the CF@sub 3@I gas plasma for the reduction of interface state density during the dielectric film etching process. By using the CF@sub 3@I plasma, a large amount of CF@sub 3@@super +@ are effectively generated without C@sub x@F@sub y@ radicals. As a result, no UV photon of 200 nm to 350 nm were observed in the plasma. Additionally, CF@sub 3@I is known as a gas for low global warming potential (GWP). For example, the GWP for CF@sub 3@I is about 1/1600 of C@sub 4@F@sub 8@ GWP. To solve the reduction of UV irradiation damage and the global warming improvement at the same time, we actually investigated the effect of the CF@sub 3@I plasma for the reduction in MIS devices. We used inductively coupled plasma with CF@sub 3@I and C@sub 4@F@sub 8@ gases. The plasma irradiation damages were evaluated by using MIS-FET as charge pumping current (Icp), and we measured UV spectra of plasma. The Icp was drastically reduced by using the CF@sub 3@I plasma comparing with C@sub 4@F@sub 8@ plasmas. In CF@sub 3@I plasma, no UV photon of 200 nm to 350 nm induced were observed.

11:20am **PS1-FrM11 Defect Generation due to UV Radiation in Plasma Etching Process***, **Y. Ishikawa,*** Tohoku University, Japan*; A. Uedono,* Tsukuba University, Japan*; S. Yamasaki,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

During the plasma process, plasma-induced ultraviolet (UV) photon generates the crystal defects in the dielectric films or in the interfaces. Especially in the SiO2 film, the UV photon generates the E' centers (Si dangling bond in the SiO2 film) in near the surface of the SiO2 film within 10 nm in depth. We had already reported that the E' center could be drastically reduced by using the pulse-time-modulated (TM) plasma. In this paper, we discussed the generation and restoration of defects during the TM plasma irradiation by using positron annihilation technique. In solid materials, the positrons are trapped at defects such as vacancy or voids with producing two 511 keV @gamma@-ray photons. To understand the situation of defects in detail, the Doppler Broadening of the @gamma@-ray photo-peak was evaluated using the S-parameter and W-parameter. S-parameter corresponds to the amount of the defects in the films, whereas, W-parameter corresponds to the electron energy distribution in the film. 500 nm of thermal SiO2 film were used, and irradiated to the Ar plasma. After the plasma irradiation, S-parameter in the case of irradiating TM plasma was the same as that in the case of using continuous wave (CW) plasma. Conversely, W-parameter after the TM plasma irradiation was much higher than that in the case of using CW plasma. These results indicate that the electron energy distributions in the SiO2 films after TM plasma irradiation are much different from that after CW plasma irradiation. Namely, different kinds of crystal defect were generated in both plasma. This result also suggests that the defects generated by TM plasma irradiation might be unstable than that generated by CW plasma. Consequently, it is speculated that the defects generated by TM plasma irradiation are easily restored through the thermal annealing. As a result, the TM plasma is much effective to eliminate generating defects due to UV irradiation during the etching processes.

11:40am **PS1-FrM12 Evaluation of Sticking Probability of Ti Atoms in Sputtering Deposition*, N. Nafarizal,* ***K. Sasaki,* Nagoya University, Japan

Knowledge on sticking probability is essential in predicting the deposition profile of a thin film inside a fine trench and a fine hole. In numerical simulations of the deposition profile, the sticking probability of metal atoms is widely assumed to be unity, but to our knowledge, there is no reliable experimental evidence of that. In this work, we evaluated the sticking probability of Ti atoms in magnetron sputtering deposition experimentally. We measured the spatial distribution of the Ti atom density in the discharge region sandwiched by a Ti target and a substrate by laser-induced fluorescence imaging spectroscopy. It was found that the Ti atom density on the substrate was not zero, clearly indicating that the sticking probability of Ti is less than unity. The magnitude of the sticking probability was evaluated by comparing the spatial distribution of the Ti density with a diffusion model proposed by Chantry (P. J. Chantry, J. Appl. Phys. 62, 1141 (1987)). The Chantry's model includes the diffusion coefficient and the gas temperature. The diffusion coefficient was obtained from a literature (D. Obhesian, et al., Opt. Comm. 32, 81 (1980)), and the gas temperature was evaluated from the Doppler-broadened linewidth of an Ar metastable state. As a result, the sticking probability was evaluated to be 0.4-0.5. The sticking probability was almost independent of the discharge power and the gas pressure. In addition, similar sticking probabilities were observed when the substrate was heated up to 520 K and when an rf bias corresponding to a self bias voltage of 200 V was applied to the substrate.

Plasma Science and Technology
Room 2011 - Session PS2-FrM

Diagnostics

Moderator: G.A. Hebner, Sandia National Laboratories

8:00am **PS2-FrM1 Substrate Temperature Sensor Measurements and Analysis in an Inductively Coupled Plasma**, *C.C. Hsu,* ***M.J. Titus****, D.B. Graves,* University of California at Berkeley

The OnWafer commercial plasma sensor system consists of sensors embedded on a thin-film battery-powered Si wafer that can enter and exit commercial plasma tools via conventional wafer-handling robotic transfer. An on-board electronics module coupled with wireless communication allows storage of process data followed by infrared uploading post-process. While this is a proven avenue for plasma process development and quasi-real time process control applications, full interpretation of sensor measurements in terms of intrinsic plasma characteristics requires validation. This talk describes the use of the OnWafer system in a university-built inductively coupled plasma (ICP) tool, equipped with a variety of plasma sensors. We describe results from a combined plasma and wafer model and compare the model predictions to both sensor measurements and plasma measurements. Measurements of wafer temperature transients (using PlasmaTemp@super TM@) are compared to a wafer and plasma model. A combination of radially-resolved Langmuir probe measurements and an ICP model is used to obtain the radial energy flux profile from the plasma to the wafer surface. Model predictions and measured transient wafer temperature profiles agree near-quantitatively, if details of the wafer and chuck characteristics are properly included. The model and measurements must include the effects of heat release due to ion-electron recombination and radical recombination at the wafer surface.

8:40am **PS2-FrM3 In-Situ Characterization of Oxygen Plasma Surface Etching by Infrared-Visible Sum Frequency Spectroscopy*, D. Farrow,* ***G.A. Hebner, E.V. Barnat,* Sandia National Laboratories

Unlike many other techniques used to characterize surfaces under plasma exposure, Infrared-visible sum frequency (IVSF) generation is a surface specific probe molecular vibrations that can be carried in situ to follow molecular interactions and plasma initiated chemistry at the interface in quasi real time. We present an in-situ characterization of octadecyltrimethoxysilane monolayers on Quartz in the presence of DC oxygen plasma based on hydrocarbon lines in the IVSF spectra as a function of plasma exposure time, voltage and oxygen pressure. These will be correlated with ellipsometry and infrared absorption measurements of samples under equivalent conditions. This test system will be used to demonstrate the unique advantages and limitations of IVSF in plasma systems.

9:00am **PS2-FrM4 Application of In Situ Plasma Analysis on Deep Trench Plasma Etch Hardware Design and Process Development**, *S. Wege, A. Steinbach, S. Barth, A. Henke, J. Sobe,* Qimonda, Dresden, Germany; ***M. Reinicke****, J.-W. Bartha,* Dresden University of Technology, Germany; *G.D. Stancu, N. Lang, J. Roepke,* Institute of Low Temperature Plasma Physics, Germany

Facing critical dimensions below 60nm requires significantly improved knowledge about the complex process mechanisms. In situ plasma analysis has been performed on different dual frequency capacitively coupled MERIE plasma reactors for DRAM technology development. High aspect ratio silicon etching mechanisms are investigated as a function of tool parameters for HBr, NF3, as well as HBr/O2/NF3 electronegative plasmas. Plasma analysis includes investigation of the influence of different plasma coupling on process results using an extensive set of planar Si and SiO2 etch rate experiments, feedstock etch gas dissociation studies, and further energy analysis of different etch species for a plasma and surface chemistry model using an in situ mass and energy plasma analyzer. For the first time, online concentration monitoring of etch species using Quantum Cascade Laser Absorption Spectroscopy is performed. Measurement results are used to extend the knowledge and insight of experimental plasma process conditions, and further as input parameters for simulations of conditions in plasma bulk and sheath, as well as structure development on wafer surface. A combined application of plasma analysis, simulation and process development on product wafers is an efficient way to optimize chamber hardware and process conditions, and to support process development.

9:20am **PS2-FrM5 2D-t Plasma Image during One Bias Period of a 2f-CCP in Ar by Emission CT*, T. Ohmori,* ***T. Kitajima, T. Makabe,* Keio University, Japan

It has been required to maintain the radial uniformity of the ion velocity distribution incident on an oxide wafer biased deeply by a LF source in a 2f-CCP. The ion velocity distribution synchronized with the sheath dynamics in front of the biased wafer is one of the critical internal plasma parameters further to control and optimize the etching profile in the next generation of the technology having an allowance within several nm. In our previous paper, we have performed a design of the functional separation in a 2f-CCP. High density plasma is sustained at a VHF (100 MHz) source, while the high energy ions are produced by a LF (500 kHz) bias source without additional discharge. We have experimentally investigated the temporal image at the central z-axis @LAMBDA@(z, t; r = 0) and at the radial position at fixed z @LAMBDA@(r, t; z), and the time-averaged image in the 2D space @LAMBDA@(r, z) in a 2f-CCP by using the CT of the optical emission from the short-lived Ar(2p@sub 1@) and Ar+(4p@super 4@D@sub 7/2@) as a probe of the plasma structure and the transport of the secondary electrons.@footnote 1@ In this work, we reconstruct an automatic CT system for the detection of the line integral of the emission in the entire space of the reactor, and demonstrate the temporal change of the 2D image @LAMBDA@(z, r, t) in a full gap of 20 mm of parallel plates during one cycle of the bias in a 2f-CCP at 25 mTor in Ar. In particular, we focus on the profile of the sheath-bulk edge and of the electrode-wall interaction as a function of bias phase in the results of the 2D-t images. @FootnoteText@ @footnote 1@T. Kitajima, Y. Takeo, N. Nakano, and T. Makabe, J. Appl. Phys. 84, 5928(1998). T. Kitajima, Y. Takeo, and T. Makabe J. Vac. Sci. Technol. A 17, 2510 (1999).

9:40am **PS2-FrM6 Advanced Plasma Sources for the Next-Generation Processing*, H.-Y. Chang,* ***S.-H. Seo,* Korea Advanced Institute of Technology (KAIST) **INVITED**

As the feature sizes of devices have shrunk in recent plasma processing, plasma sources operating at low pressures (1-100mTorr) have been required for formation of good anisotropic patterns, high throughput, and damage-free process. Recently, the main subjects in developing a new plasma source have been the attainment of good uniformity in large area, the control of plasma parameters for the process optimization, and the development of new application area. Among several plasma sources, inductively coupled plasma (ICP), capacitively coupled plasma (CCP) and the ultra low electron temperature plasma sources have been the focus of keen interest as the new and efficient sources for many plasma processing including the semiconductor manufacturing because these have many attractive aspects such as their simple apparatus, relatively efficient plasma generation, good special uniformity, low and independently controlled ion energy, and scalability to large-area plasma sources.@footnote 1@ In this presentation, a couple of newly developing plasma sources will be introduced with the brief review of the electron heating mechanisms in plasma sources along with the recent experimental and theoretical results focusing on the electron energy distribution function (EEDF), ion energy

distribution function(IEDF) and rf fields in the collisionless regime.@footnote 2,3@ In addition, some examples for the control of plasma parameters through adjusting rf frequency and power, operating pressure, gas mixing ratio,@footnote 4@ and other external parameters in order to optimize the process will be presented. @FootnoteText@@footnote 1@ S.H.Seo, C.W. Chung and H.Y.Chang: Surf and Coating Tech. 131(2000) 1-11 @footnote 2@ V.A.Godyak : Plasma Sources Sci. Technol. 3,169(1994) @footnote 3@ C.W.Chung and H.Y.Chang : Phys.Rev.Lett. @footnote 4@ K.H.Bai and H.Y .Chang: Physics of Plasma

10:20am **PS2-FrM8 Real-time, Noninvasive Monitoring of Ion Energy and Ion Current at Insulating Electrodes*, M.A. Sobolewski,*** National Institute of Standards and Technology

The dc self bias voltage is often monitored during plasma processing because it provides a rough estimate of ion bombardment energies. However, many industrial plasma reactors are now equipped with electrostatic chucks, which have a large dc impedance that makes dc bias measurements impossible. A chuck may also have a large rf impedance which produces a significant rf voltage drop across the chuck. In this study chuck impedance effects were investigated in an inductively coupled plasma reactor by incorporating insulating structures into the rf-biased lower electrode. Measurement methods were developed to characterize the capacitive impedance of the insulating electrode itself and the combined impedance of the electrode plus the wafer. This impedance was included in a numerical model of the plasma and its sheaths, and the combined model was used to analyze measured rf bias current and voltage waveforms. This approach allows a real-time, noninvasive monitoring technique developed for bare metallic electrodes@footnote 1,2@ to be extended to insulating electrodes, including electrostatic chucks. The technique not only determines the dc self bias voltage present on the surface of the wafer or chuck, but also the time-dependent plasma potential and sheath voltages, the total ion current, and the ion energy distributions at the wafer or chuck surface. @FootnoteText@ @footnote 1@ M. A. Sobolewski, J. Appl. Phys. 95, 4593 (2004). @footnote 2@ M. A. Sobolewski, J. Appl. Phys. 97, 033301 (2005).

10:40am **PS2-FrM9 The Ion Energy Distributions in a High Power Impulse Magnetron Discharge*, J. Bohlmark,*** Chemfilt Ionsputtering AB, Sweden*; M. Lattemann,* Linköping Univ., Sweden*; J.T. Gudmundsson,* Univ. of Iceland, Iceland*; A.P. Ehiasarian,* Sheffield Hallam Univ., UK*; Y.A. Gonzalvo,* Hiden Analytical Ltd., UK*; J. Carlsson,* Chemfilt Ionsputtering AB, Sweden*; N. Brenning,* Royal Institute of Tech., Sweden*; D. Lundin, U. Helmersson,* Linköping Univ., Sweden

We report on the ion energy distributions of sputtered and ionized Ti and the sputtering gas (Ar and N2) for a high power impulse magnetron sputtering (HIPIMS) discharge. High power pulses were applied to a conventional planar circular magnetron Ti target. The peak power on the target surface was 1-2 kW/cm@super 2@ with a duty factor of about 0.5 %. Time resolved, and time averaged ion energy distributions were recorded with an energy resolving quadrupole mass spectrometer. The ion energy distributions are very broad during the active phase of the discharge with maximum detected energy of 100 eV, but quickly narrows as the pulse is switched off. The time averaged measurements show that about 50 % of the Ti ions have energies over 20 eV. The broad nature of the distributions together with the fact that the Ti and gas ion distributions peak at different energies during the active phase of the discharge excludes acceleration between the plasma potential and the grounded spectrometer as explanation for the energetic ions. Instead we suggest that the shape of the distributions can be explained by a combination of a strong pressure increase in front of the target and ion acceleration by electric field instabilities. The composition of the ion flux was also determined, and reveals a high metal fraction. During the most intense moment of the discharge, the ionic flux consisted of approximately 50 % Ti1+, 24 % Ti2+, 23 % Ar1+, and 3 % Ar2+ ions. We are planning to continue the study by investigating the effect of the energetic plasma on thin film growth. It is expected that HIPIMS can be used as a tool for film densification where a substrate bias is not easily applied, which opens up for improved device or component performances.

11:00am **PS2-FrM10 Monitoring of Electron Density in Plasma Reactor with Frequency Shift Probe*, K. Nakamura,*** Chubu University, Japan*; H. Sugai,* Nagoya University, Japan

A plane type of frequency shift (FS) probe for monitoring electron density in reactive plasmas was developed with modification of the hairpin probe.@footnote 1@ The FS probe is connected to a network analyzer to detect reflection from the probing plane antenna located at an inner surface of the chamber. The reflection becomes minimum at a certain frequency due to resonance at the antenna, and the resonant frequency shifts from f0 for vacuum without plasma to higher frequency f in the presence of the plasma because of a decrease in permittivity. The frequency blue shift (f-f@sub 0@) gives the absolute electron density ne according to ne (x10@super 10@cm@super -3@) =[f@super 2@-f@sub 0@@super 2@]/0.81 in unit of GHz for f and f@sub 0@. In principle, the FS probe is based on volume wave resonance while a previouly-proposed surface wave (SW) probe relies on surface wave resonance.@footnote 2@ In comparison to the SW probe, the plane FS probe has various advantages. The FS probe can be installed on a reactor wall surface, thus minimizing the disturbance to processing plasmas. Furthermore, since the resonance cavity of the FS probe is formed at the plane antenna itself, the resonance frequency can be measured easily in a wide range of the discharge conditions. The characteristics of FS probe were examined in an ICP reactor as functions of the RF power and the discharge pressure, and the experiments revealed that the wall-installed FS probe could monitor relative variations of electron densities in the bulk plasma.@FootnoteText@ @footnote 1@ R. B. Piejak et al. J. Appl. Phys. 95 (2004) 3785.@footnote 2@ H. Kokura et al: Jpn. J. Appl. Phys. 38 (1999) 5262.

11:20am **PS2-FrM11 Energy Distribution and Flux of Fast Neutrals and Residual Ions Extracted out of High Aspect-Ratio Holes in a Neutral Beam Source*, A. Ranjan,*** *V.M. Donnelly, D.J. Economou,* University of Houston

The energy distribution and flux of fast neutrals and residual ions extracted from a neutral beam source were measured. Positive ions generated in an inductively coupled argon plasma were extracted through a metal grid with high aspect ratio holes. Ions suffering grazing angle collisions with the inside surface of the grid holes turned into fast neutrals. The neutral energy distribution shifted to lower energies compared to the corresponding residual ion energy distribution. The neutralization efficiency increased with power, decreased with the imposed plasma potential (controlled with a boundary voltage) and, for thin neutralization grids, was almost independent of plasma gas pressure. The residual ion flux decreased with increasing hole diameter and hole aspect ratio. The fast neutral flux first increased and then dropped as the hole diameter was increased. These results were explained based on plasma molding inside the grid holes. The effect of surface roughness of the grid walls on the energy distribution and flux of fast neutrals and residual ions was also studied. A nearly atomically smooth grid was fabricated from a closely-spaced stack of polished Si (100) wafer strips. With this grid, a small fraction of fast neutrals was observed at energies nearly equal to the maximum ion energy. For the metal grids, with rougher surfaces, the highest energy neutrals were well below the maximum ion energy. These observations will be discussed in terms of the type of scattering (specular vs. non-specular) that occurs when ions are converted into fast neutrals.

11:40am **PS2-FrM12 Electron Energy Distribution Function Measurement in Radio-Frequency Plasmas Produced in Insulated Vessels*, H. Shindo,*** *K. Kusaba,* Tokai University, Japan

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

further positions from the antenna the energy distribution became Maxwellian. This feature has also been reported recently. This change in the electron energy distribution found in ICP was very systematic with the gas pressures and the distances from the antenna.

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