# Monday Morning, October 15, 2007

## Plasma Science and Technology

## Room: 606 - Session PS1-MoM

## Plasma Modeling

**Moderator:** C.C. Hsu, University of California at Los Angeles

8:00am **PS1-MoM1 Mechanisms of Surface Roughness Formation and Evolution during Plasma Etching**, ***G. Kokkoris***, *V. Constantoudis, G. Boulousis, P. Angelikopoulos, E. Gogolides*, NSCR Demokritos, Greece

The control and understanding of roughness formation during plasma etching is of primary importance in micro- and nano-fabrication technology. In one hand, the roughness of the surfaces of fabricated features may degrade electrical, optical or other device performance. On the other hand, there are beneficial effects of high surface roughness, e.g., in the fabrication of super-hydrophobic surfaces.[1] In this work, a stochastic (Monte Carlo) simulator is used for the study of the surface roughness formation and evolution during plasma etching. The etched film is represented by cells. Shadowing and reemission of particles are taken into account. The trajectory of each particle is calculated until sticking on a cell. The interaction of the particles with the cells is defined by the sticking probability and the etching yield. The focus of the simulation is on Si etching by fluorine-containing plasmas. A common finding of past works devoted to investigation of roughness origins on plasma etched Si surfaces was the increase of the surface roughness, i.e., the root mean square roughness, versus etching time.[2,3,4] In a previous work[2], by using a (1+1)D stochastic simulator, we also demonstrated that the experimentally observed dual scale roughness is captured by a simple model including reactive neutral species, ions and etch inhibitors; the latter may come from sputtering of the electrode and the reactor-wall (hard inhibitors). In this work, we attempt to quantitatively reproduce all surface roughness parameters, e.g., correlation length, by a) refining model parameters, b) including another type of etch inhibitors (soft inhibitors) produced in the bulk phase of the plasma reactor, c) taking into account surface diffusion, and d) using a (2+1)D simulation tool. Atomic Force Microscope (AFM) images of Si surfaces etched by $SF_6$ plasma are characterized and compared to the simulation results.

[1] N. Vourdas, A. Tserepi, E. Gogolides, Nanotechnology 18,125304(2007).
[2] P. Angelikopoulos, V. Constantoudis, G. Kokkoris, G. Mpoulousis, P. Xidi, and E. Gogolides, AVS 53rd, San Francisco, USA, November 12-17, 2006.
[3] Y.-P. Zhao, J. T. Drotar, G. C. Wang, and T. M. Lu, Phys. Rev. Lett. 82, 4882 (1999).
[4] E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, and V. Constantoudis, Microelectron. Eng. 73-74, 312 (2004).

8:20am **PS1-MoM2 Molecular Dynamics Simulation of Hydrogen Induced Damage to Si and $SiO_2$ Substrates during Reactive Ion Etching (RIE) Processes**, ***T. Takizawa***, Osaka University, Japan, *S. Kobayashi, T. Tatsumi,* Sony Corp., Japan, *S. Hamagushi*, Osaka University, Japan

As the dimensions of transistors diminish in Ultra-Large-Scale Integrated (ULSI) circuits, "small" damage to the substrate materials caused by plasma etching during chip fabrication processes can have adverse effects on chip performance. In the present work, we investigate damage to Si and $SiO_2$ caused by energetic hydrogen injections in, for example, a reactive ion etching (RIE) process of Si with a gas containing HBr, using classical molecular dynamics (MD) simulations. In this work, we performed MD simulations of energetic hydrogen injections into Si and $SiO_2$ substrates and measured penetration depths of H atoms and also reaction characteristics, e.g., bond formation of injected hydrogen with substrate atoms, as functions of the injection energy in the range of 50 -200eV. As injected species, we examined both atomic and molecular hydrogen, i.e., H and $H_2$. It is usually difficult to determines penetration (implant) depth profiles for hydrogen experimentally, so these MD simulation may give good insight into such problems. It was found that the average penetration depth is essentially proportional to the injection energy. For Si and $SiO_2$ substrates, hydrogen is found to penetrate deeper in Si than in $SiO_2$ for the same injection energies. The penetration depth has been also found to depend only on the impact energy of each H atom whether it is injected as a hydrogen atomic or part of a hydrogen molecule. As to reaction characteristics, in the case of a $SiO_2$ substrate, the majority of injected hydrogen atoms are bound with substrate oxygen atoms, generating hydroxyl groups. In this case, $H_2$ molecules are hardly formed. Similarly, in the case of a Si substrate, the majority of injected hydrogen atoms form Si-H bonds. However, in this case, $H_2$ molecules can be also generated in the Si bulk. These MD simulations are based on a newly developed classical interatomic potential functions for Si, C, O, F, and H systems. The model potential functions were developed from data obtained from the density functional calculations based on Gaussian03 (B3LYP), a first-principle simulation code. We are also in the process of evaluating sputtering yields of SiOCH by energetic injections of fluorocarbon radical ions, i.e., $CF_x^+$. Details of such reactions will be also discussed.

8:40am **PS1-MoM3 Vertically Integrated Computer Aided Design for Devices Process**, ***T. Makabe****, Keio University, Japan **INVITED**

We had our opportunity to propose a relaxation continuum (RCT) model for a low temperature radio-frequency plasma in 1988 in GEC.[1] In 2000 we presented a vertically integrated computer aided design for device processes (VicAddress) in RGD.[2] With the aid of VicAddress described by a hybrid model consisting of the RCT model and particle model, a series of modeling has been carried out for the prediction and the design for a space- and time-resolved plasma structure, sheath dynamics of reactive species, a feature profile evolution, and the damage to a lower level device element during plasma etching.[3] These are a typical example of the multi-scale system. In this talk, we will review the dry etching of dielectric SiO2 in CF4/Ar[4] and organic low-k material in N2/H2[5] under competitive processes among charging, deposition, and etching at each of local positions of a geometrical structure by considering two-layers, intrinsic (or mixing layer) and an overlaying polymer layer in a two-frequency capacitively coupled plasma on the basis of a database of etching yield. Also a Si deep etching with several hundreds of micrometers such that used in MEMS fabrication is predicted under an effect of plasma molding, and the effect of ions, F-radicals, and oxygen radicals on the feature profile is investigated in SF6/O2 in 2f-CCP.[6]

[1]T. Makabe, 41st GEC (Minneapolis)(1988).
[2]T. Makabe, 22nd Int. Symposium on Rarefied Gas Dynamics (Sydney) (2000).
[3]T. Makabe and Z. Petrovic, "Plasma Electronics: Applications in Microelectronic Device Fabrication", Taylor & Francis (New York) (2006).
[4]T. Shimada, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys. 45, 8876 (2006).
[5]K. Ishihara, T. Shimada, T. Yagisawa, and T. Makabe, Plasma Physics and Controlled Fusion, 48, B99 (2006).
[6]F. Hamaoka, T. Yagisawa, and T. Makabe, IEEE TPS (accepted for publication).

9:20am **PS1-MoM5 Ion Energy and Angular Distributions into Small Features in Plasma Etching Reactors: The Wafer- Focus Ring Gap[1]**, ***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 across the entire substrate. This goal is often complicated by the necessary mechanical gap between the edge of the wafer and the terminating structures, such as the focus ring. Plasma penetration into the gap is of concern due to the likelihood of depositing particle forming materials and erosion. We previously showed that the ratio of the Debye length (or sheath thickness) to the width of the wafer-focus ring gap (WFG) is an important parameter: small ratios allow penetration of plasma species in the WFG.[2] As a result, orientation of the electric field, ion trajectories and ion energy and angular (IEAD) distributions are functions of this ratio as well as the details of the geometries and materials. In this talk, we extend that study with a computational investigation of ion energy and angular distributions into the WFG. The model used in this investigation is a 2-dimensional plasma hydrodynamics model utilizing an unstructured mesh to resolve the small structures of the WFG. A Monte Carlo simulation was added to the model to track the trajectories of the ions and neutrals while capturing their gas phase collisions and interactions with the surface. Electric potentials as a function of phase from the unstructured mesh are interpolated onto a fine rectilinear capable of resolving the WFG to facilitate a rapidly executing MCS. The consequences of voltage waveform, frequency and geometry of the WFG on IEADs inside the gap (e.g., incident on the lower edge of the wafer bevel) will be discussed for RIE plasmas sustained in fluorocarbon gas mixtures at tens of mTorr.

[1] Work supported by the Semiconductor Research Corp. and the National Science Foundation.
[2] N. Y. Babaeva and M. J. Kushner, "Penetration of Plasma into the Wafer-Focus Ring Gap in Capacitively Coupled Plasmas", to appear in J. Appl. Phys. (2007).

9:40am **PS1-MoM6 Effect of Dual Frequency Bias on Ion Energy and Angular Distribution and Feature Profile in a Capacitively Coupled Plasma Reactor**, ***K. Bera***, *S. Rauf, K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma reactors are commonly used in dry etch processes. Control of ion energy and angular distribution function (IEADF) is key to achieving desired etch profile in a plasma reactor. Dual frequency bias combining medium frequency (MF) and high frequency (HF) can be used to modulate the ion energy distribution. Understanding the effect of

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MF and HF mixing on IEADF is crucial for etch profile control. MF and HF bias are mixed in this investigation, and the mixing effect is characterized for IEADF and etch profile. Plasma simulations have been conducted using the Hybrid Plasma Equipment Model, while a string-based model is used for feature profile simulations. Interaction between ions and electric field modulation across the sheath determined the ion energy and angular distribution. A mono-energetic peak is observed using HF bias while ion energy distribution is broader using MF bias. DC bias is comparable at HF and MF bias for a given RF voltage. Plasma density with MF bias is smaller than that with HF bias. Mixing of MF and HF leads to lower DC bias and lower ion energy. The plasma density distribution and sheath structure are observed to change as the MF voltage is increased relative to HF bias for a given total MF + HF voltage. Ion flux at the wafer is determined by the plasma profile while the local sheath dynamics control the ion energy and angular distribution. Ion flux and IEADF are calculated near the center, middle and edge of the wafer, which are then input into a feature profile model. The feature profile model includes mechanisms for Si and mask etching. The etch depth and selectivity are calculated at the above three locations on the wafer for various mixtures of MF and HF biases. The etch profile is tuned using the mixing of MF with HF bias. Based on etch depth variation across the wafer, etch profile uniformity is calculated. Profile tilting is observed at locations where sheath is non-planar and the ion angular distribution is asymmetric. Various process-kits are evaluated to minimize profile tilting.

10:20am **PS1-MoM8 Modeling of a Dual-Coil and Dual-Flow Inductively Coupled Plasma Reactor**, *C.C. Hsu, **V. Le**, J.P. Chang*, University of California at Los Angeles

The ion flux spatial profile and the etching by-products transportation are among the most important characteristics for plasma processes. The above characteristics need to be well-tailored in order to achieve the desired etching process performance, such as the uniformity and the etched feature profile. A numerical model has been developed to investigate how the processing parameters affect the plasma characteristics and how these characteristics in turn alter the spatial distribution of the plasma species. This numerical model is a two dimensional fluid model of an inductively coupled plasma in mixtures of chlorine, oxygen, and argon. It has been setup to resemble a simplified commercial etching tool, AMAT DPS-II$^{TM}$, used for 300 mm wafer shallow trench isolation (STI) processes. This tool is equipped with dual-coil and dual-flow arrangements allowing for additional etching process control. It was shown in this model that the spatial profile of the inductively coupled power deposition can be altered by changing the current ratio of the outer and the inner coils of the dual-coil (DC ratio). This change in turn altered the spatial profile of the ion flux and the plasma species densities. For example, by increasing the DC ratio, the center-to-edge ratio of the Cl radical and the ion flux to the wafer surface decreased. The model was then used to interpret the spatial variation and the variation among different operating conditions of a number of STI etched feature profiles obtained by an AMAT DPS-II$^{TM}$ with chlorine-based chemistries. The model qualitatively explained the spatial variation of the etched depth and the side wall angles of the etched profiles. One example was to explain the consistently positive center-to-edge variation of the etched profile sidewall angel using the center-high by-products density obtained by this fluid model. The effect of the flow to the dual-flow gas feed on the by-products transportation and distribution will also be discussed.

10:40am **PS1-MoM9 Prediction of Feature Profile Evolution of Deep Si Etching under Effect of Plasma Molding in 2f-CCP in $SF_6/O_2$**, ***F. Hamaoka**, T.Y. Yagisawa, T. Makabe*, Keio University, Japan

Deep-RIE is widely used in MEMS fabrication. In large-scale etching, plasma molding is one of the important issues.[1] In our previous study, the influence of the ion transport under the distorted electric field, i.e., plasma molding, on the anisotropic Si etching was numerically investigated without considering the neutral reaction.[2] In this study, we numerically investigate the feature profile evolution of deep Si etching on the MEMS scale in a 2f-CCP in $SF_6/O_2$ under competition between Si etching by ions and F radicals and passivation layer formation by O radicals, including the effect of plasma molding. In $SF_6(83\%)/O_2$ at 300 mTorr, for only physical $SF_5^+$ ion etching of Si, the etching is enhanced at the bottom corner due to the distorted ion incidence on the wafer under the plasma molding. In the case of RIE caused by both $SF_5^+$ ions and F radicals without passivation layer formation, the influence of the plasma molding on the feature profile is not observed because of a much higher etching rate of Si by F radicals than that by $SF_5^+$. However, the bowed and undercut profiles appear significantly at the sidewall and near the silicon-mask interface. Finally, we estimate the feature profile evolution of Si by RIE with the passivation layer formed by O radicals. Under the presence of the plasma molding, the removal of the passivation layer by energetic ions at the bottom corner is strengthened by the effect of excess ion flux with distorted angular distribution. On the other hand, an insufficient amount of ions leads to less efficient removing the passivation layer at the center of the bottom. The chemical etching rate of Si layer for F radicals is much higher than that of passivation layer. Thus, when the passivation layer is removed by $SF_5^+$ion impact, the etching of Si is enhanced by addition of F radicals. As a result, this indicates that anisotropy of the etching profile is not achieved especially at the bottom in $SF_6(83\%)/O_2$ at 300 mTorr.[3] Further investigation will be given for influence of the percentage of Oxygen on anisotropic feature profile on the MEMS scale in the 2f-CCP system.

[1]D. Kim and D. J. Economou, IEEE. Trans. Plasma Sci., vol. 30, no. 5, pp. 2048-2058, 2002.
[2]F. Hamaoka, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys., vol. 46, no. 5A, pp. 3059-3065, 2007.
[3] -, IEEE Trans. Plasma Sci., (accepted for publication), Oct 2007.

11:00am **PS1-MoM10 Prediction of Feature Profile Evolution in Shallow Trench Isolation Etching**, ***J. Hoang**, C.C. Hsu, J.P. Chang*, University of California at Los Angeles

Predictive modeling of feature profile evolution is critical to understand the complex plasma-surface interactions and aid the design of etch chemistry and development of etch systems. In this work, a direct simulation Monte Carlo (DSMC) method is used to develop a simulator that predicts profile evolution during shallow trench isolation etch (STIE) in Cl-based plasmas. Due to the discretized cells inherent in the model, a segmented surface advancement algorithm was developed to capture surface normals and particle fluxes. Plasma parameters such as particle densities and mean ion energy are determined from a reactor scale model, while ion energy distribution (IED) and ion angular distribution (IAD) are verified by a particle-in-cell (PIC) model.[1] A fractional factorial design of experiments determined major processing parameters affecting profile evolution in a $Cl_2$, $O_2$, and $N_2$ plasma in a dual coil inductively coupled plasma reactor. Out of seven parameters investigated, chamber pressure and DC ratio (current ratio of inner and outer coils) had the most effect on the feature side wall angle (SWA), one of the most critical parameters defining the success of STIE. Additional experiments were performed to assess the effect of $O_2$ addition as well as to ascertain the effects of source power and DC ratio. Scanning electron microscopy (SEM) was used to assess the profile evolution in various plasma chemistries under different etch conditions. Slight microtrenching was observed in features etched by pure chlorine (no $O_2$) and was accurately predicted by the profile simulator, sampling only ions ($Cl^+$), neutral etchants (Cl), and a minute ratio of neutral passivants (e.g. $SiCl_2$). Changes in plasma density and substrate bias (translating to ion energy) were found to significantly alter the sidewall tapering and etch depth. The profile simulator captured these changes by determining the full-width half maximum of the IAD as a function of substrate bias and adjusting the neutral to ion ratio which is affected by pressure and source power. The erosion of the hard mask during STIE was found to occur in a high density plasma under high substrate bias, affirming an etching threshold energy of the hard mask, and the simulator successfully predicted the double facets on the hard mask and the resulting profile.

[1]A. C. F. Wu, M. A. Lieberman, and J. P. Verboncoeur, Journal of Applied Physics 101, 056105 (2007).

11:20am **PS1-MoM11 Investigation of Source and Bias Pulsing for High Aspect Ratio Silicon Etching**, ***G. Wenig**, A. Kersch, W. Jacobs, S. Barth, A. Henke, J. Sobe, A. Steinbach, S. Wege*, Qimonda, Germany, *M. Reinicke*, Dresden University of Technology, Germany

Silicon etching based on a HBr/O2/NF3 plasma generated in a dual (2 and 60MHz) 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 contribution a high aspect ratio silicon etch selective to an oxide mask is studied with respect to the influence of pulsing the rf sources on the ion energy and angular distributions. Particle-in-cell and efficient hybrid fluid-kinetic simulations are used to investigate the consequences of source and bias pulsing. Both methods use identical ion-neutral collision models. The required differential cross sections have been computed ab initio. Charge exchange processes are treated with a constant charge exchange probability. The resulting ion and neutral distributions are used as input for a Monte Carlo simulation of particle transport in the trench. Pulsing frequencies, duty cycles, and phase shifts are varied separately. Modeling results and experimental data show the beneficial effects of pulsing on etch results.

11:40am **PS1-MoM12 Global Plasma Simulations using Dynamically Generated Chemical Models**, ***J.J. Munro**, J. Tennyson*, University College London, England

Extensive molecular data is a key requirement in understanding modern technical plasmas. Here we present a method for coupling molecular data with chemical models and a global plasma simulation to enable rapid testing and evaluation of new plasmas. A global plasma model (GLOBAL_KIN[1])

is extended using an expert system 'Quantemol-P' to enable ad-hoc simulations using new plasma recipes. A set of atomic and molecular species to be considered in the plasma simulation is specified by the user. The expert system generates a complete set of reaction pathways for both the gas and surface reactions in a plasma. This set is pruned by discarding un-physical reactions and reaction data not appropriate to technical plasmas. Where data exists, a rate is calculated for the reaction at the plasma temperature so its importance can be evaluated. Where no data exists, a set of heuristics is used (based upon reaction type) to evaluate the reaction's importance. A user can adjust the species, gas phase reactions, surface reactions and plasma properties to control the simulation. The reaction list is populated with a database of molecular parameters and cross-sections; missing data can be calculated using a further expert system 'Quantemol-N'.[2] This applies the R-Matrix method, which has proven highly accurate for electron-molecule interactions.[3] In instances where this R-Matrix method does not apply, other methods such as the Binary Encounter Bethe model[4] maximize the range of cross-section data available. The method allows for rapid investigation of new plasma recipes with a greater level of flexibility than previously achievable. A simple plasma-etch example is presented to demonstrate the system.

[1]D.S. Stafford and M.J. Kushner, O2(1-delta) Production in He/O2 Mixtures in Flowing Low Pressure Plasmas, J. Appl. Phys. 96, 2451(2004).

[2]J. Tennyson, D.B. Brown, J.J. Munro, I. Rozum, H.N. Varambhia and N. Vinci, Quantemol-N: an expert system for performing electron molecule collision calculations using the R-matrix method, J. Phys. Conf. Series, (in press).

[3]H.N. Varambhia and J. Tennyson, Electron collision with HCN and HNC molecules using the R-matrix method, J. Phys. B: At. Mol. Opt. Phys. 40, 1211-1223 (2007).

[4]W. Hwang, Y.-K. Kim and M.E. Rudd, New model for electron-impact cross sections of molecules, J. Chem. Phys. 104(8), 2956-2966 (1996).

## Plasma Science and Technology

## Room: 607 - Session PS2+MS-MoM

## Plasma Etching for Advanced Interconnects I

**Moderator:** V. Ku, Applied Materials

8:00am **PS2+MS-MoM1 Challenges for Microwave Plasma Etching of Low-k Dielectrics**, ***T. Nozawa***, *M. Inoue, T. Nishizuka*, Tokyo Electron LTD Japan **INVITED**

Meeting post 32 nm etch process integration requirements with porous SiCOH and conventional plasma sources is a challenge as the SiCOH surface is decomposed by reactions induced by electron, ion, radical and UV radiation exposure. This exposure is inherent to most plasma systems making it difficult to achieve both high precision and damage free etching. Neutral beam etching has been developed to provide ion and UV radiation free and therefore damage free etching processes. Neutral beam etching by itself lacks the benefits of energy and chemistry control afforded by in-situ plasma processes. A Radial Line Slot Antenna (RLSA) driven surface-wave-plasma at 2.45GHz generates very high density plasma with high electron temperature in a region limited to just below the dielectric plate through which microwave pass. Both chemistry and energy control are achieved with the RLSA configuration. Plasma is transported to the wafer by diffusive transport through a low electron temperature region. An electronegative precursor gas (e.g., C4F8) is injected into the low electron temperature region so that dissociation is not excessive and a substantial negative ion population is generated near the wafer. An RF bias frequency 400kHz through the wafer provides ion acceleration without plasma generation. The combination of the low electron temperature electronegative downstream plasma with the low driving frequency facilitates charge damage free etching for all process conditions. Another consequence of the combination of plasma conditions near the electrode is that physical damage of SiCOH material is eliminated and k-value increase is minimized. This is achieved through dissociation control which results in the population reduction of small very reactive species such as H* and F* and the retention of sidewall polymer integrity. The unique plasma characteristics of the RLSA system will be described in this presentation with an emphasis on process performance for post 32 nm node CMOS fabrication.

8:40am **PS2+MS-MoM3 High Frequency Capacitively Coupled Plasma for Low Ion Energy Dual Damascene Etching**, ***A. Marakhtanov***, *E.A. Hudson, K. Takeshita, O. Turmel*, Lam Research Corp.

Capacitively coupled discharges are widely used for semiconductor processing, especially in the area of dielectric etching. With a wide range of film materials and complex stacks including multiple mask layers, advanced dielectric etch processes require tight control of plasma parameters, such as ion flux, radical composition, and ion energy distribution (IED). This paper presents IED measurements and patterned-wafer etch results as a function of RF bias excitation frequency applied to the wafer electrode. The aim is to produce the optimal IED for etching of soft materials, such as low-k dielectrics commonly used in Dual Damascene interconnect schemes. One key challenge arises in the trench etch step, which requires a vertical etch profile in the low-k film. But the process must avoid corner faceting of any exposed via holes or of the hard mask layer which defines the initial trench pattern. Faceting would cause an increase in via or trench critical dimension, respectively. The competing requirements of vertical profile and minimal faceting define a fairly narrow range of acceptable ion energies for the process. If power is held constant, higher RF driving frequencies typically produce plasmas with higher densities and lower potentials, and enable operation at lower pressure. Both the mean ion energy and width of the IED reaching the wafer tend to decrease as the wafer bias frequency increases. For frequencies too low, the width of the IED is too large and faceting is induced by the high energy ions. For frequencies too high, the mean IED is too low to etch the low-k film with a vertical profile and acceptable rate. Results show that the necessary IED for these applications can be obtained by applying 60MHz to the wafer electrode.

9:00am **PS2+MS-MoM4 Energy Distribution of Bombarding Ions, Etch Selectivity and Profile Control in Plasma Etching of Dielectrics**, ***F.L. Buzzi***, *Y.-H. Ting, A.E. Wendt*, University of Wisconsin-Madison

The energy distribution of bombarding ions during plasma etching of dielectrics for microelectronics manufacturing affects both selectivity to photoresist and the profile shape of the etched feature. Here we examine the role of ion bombardment making use of an ability to produce either a narrow ion energy distribution (IED) at a specified energy, or a two-peaked distribution in which the energy and relative flux of the two peaks can be controlled. A system has been developed for manipulating the IED at the substrate during plasma etching by controlling the voltage bias waveform of the RF bias applied to the substrate. The output of a waveform generator drives a broadband power amplifier connected to the electrode, and is programmed in an iterative process to produce the desired substrate wave form. The iterative feedback process has recently been automated so that arbitrary waveforms can be quickly achieved. Waveforms to produce ions at the substrate with energies greater than 500 eV in single-peaked or two-peaked IEDs are now routinely produced, and are applied to etching of silicon dioxide in fluorocarbon-based gas mixtures. Prior studies with a single-peaked IED at energies below 200 eV showed significant improvements in etch selectivity compared to a sinusoidal bias producing a broad IEDF (Wang and Wendt, 2001, Silapunt et al., 2003). In this study, we will report on a systematic characterization of IED effects on blanket and patterned wafers. Results include the following: 1) effect of ion energy on photoresist and oxide etch rates for the narrow single-peaked IED at high energy, 2) effect of ion energy on photoresist roughening/distortion, to explore evidence of improved performance with higher energy ions, and 3) systematic study of the asymmetric bimodal IEDs as a function of the relative ion fluxes at the two energies, to examine the effect on etch rates for oxide and photoresist and etched feature profiles. The plasma system is equipped with a helicon plasma source operating at 13.56 MHz. The substrate electrode accommodates 4" diameter wafers, and is equipped with helium backside cooling and a thin film laser interferometer to monitor etch rates of blanket films. The chamber walls are heated externally to minimize process drift associated with wall temperature changes during plasma operation.

9:20am **PS2+MS-MoM5 Etch Plasma Chemistry and Film Variability Effects on Dual Damascene Patterning of Porous Ultra-low k Materials**, ***C.B. Labelle***, AMD, Inc., *J. Arnold*, IBM Research, *H. Wendt*, Infineon Tech., *R.P. Srivastava*, Chartered Semicon. Mfg Ltd., *K. Kumar, Y. Choi, H. Yusuff, S. Molis, C. Parks, C. Dziobkowski, M. Chace, A. Passano, L. Tai*, IBM Microelectronics, *D. Kioussis*, AMD, Inc., *J. Yamartino, D. Restaino, L. Nicholson*, IBM Microelectronics

Porous ultra low k dielectrics ($k < 2.5$) are being integrated into current and future technology nodes. A large focus of the integration of these films has been on the sensitivity of the films to compositional modification (i.e., carbon depletion) during resist strip in the dual damascene patterning scheme. As porous ultra low k dielectric strip processes have evolved and matured, new sensitivities have emerged which affect successful integration. This paper will discuss a case where, in a via-first-trench-last dual damascene integration scheme, the plasma chemistry used during via etch has been found to affect the profiles after trench etch when etching porous ultra low k dielectrics ("ULK via/trench interaction"). Modifications to the via etch plasma chemistry can be made to bring the trench profile back to target, but repeatability of the success of these workarounds is key. Variability in the film composition through the bulk of the film can also instigate post-etch profile changes or exacerbate the etch plasma-induced via/trench interaction. Data will be shown demonstrating the sensitivity of

the etch processes to film composition variability. Possible mechanisms for the ULK via/trench interaction will also be discussed.

9:40am **PS2+MS-MoM6 Surface Roughening Mechanisms during Porous SiOCH Etching Processes**, *F. Bailly,* CNRS/IMN - France, ***T. David***, CEA/LETI-MINATEC - France, *T. Chevolleau, M. Darnon,* CNRS/LTM - France, *C. Cardinaud*, CNRS/IMN - France

Introducing dual damascene structures for the interconnections has been a means of improving their electrical performances. However, lowering the effective dielectric constant remains a major stake. Increase the porosity of the dielectric material or remove the trench bottom etch stop layer are some solutions. As a result, the trench etch process is stopped into the porous material which may lead to a tricky trench bottom roughness. In addition, sidewall metal diffusion barriers have to be thinned down to keep the copper line resistance low. In this context, the trench bottom roughness may also affect metal barrier coverage. In this study, roughness of dielectric materials is characterized by SEM and AFM after partial etching. Dielectric etching is known to be controlled by the thickness and composition of a fluorocarbon overlayer which depends on the plasma characteristics (etch chemistry…) and on the materials properties (composition, porosity,…). Thereby, in order to understand the mechanisms controlling the porous SiOCH roughening, different etch plasmas have been performed on materials with different percentages of porosity (7, 25 and 30%). For a high polymerizing ($CF_4$/Ar/$CH_2F_2$), a low polymerizing ($CF_4$/Ar) and a pure physical sputtering plasma (Ar), surface composition has been characterized by quasi in situ XPS and the roughness has been studied as a function of the etched thickness. Those experiments highlight different trends. Firstly, the 7 % porous SiOCH does not exhibit any significant roughness whatever the etching plasma (rms roughness = 0.5nm). Secondly, porous SiOCH with a higher porosity (25 and 30%) is roughened when exposed to fluorocarbon based plasmas. The resulting roughness increases linearly versus the etched thickness in the range of a tenth of nanometers. This increase is fast when the concentration of fluorocarboned species at the etched surface is low, while a higher amount of fluorocarboned species limits it. At last, sputtering of porous SiOCH using a pure Ar plasma, namely the absence of fluorocarboned species at the etched surface, leads to a surface as smooth as the pristine material (rms roughness = 0.2 nm). Those results highlight the critical role of porosity and the presence of fluorocarboned species on the dielectric surface roughening. On the basis of those observations, a hypothesis will be proposed for the initiation and maintaining of the dielectric roughness.

10:20am **PS2+MS-MoM8 Design for Manufacturability through Design-Process Integration**, ***A. Neureuther***, University of California, Berkeley **INVITED**

Exploratory prototype Design for Manufacturing (DFM) tools and methodologies are described. Examples will include new platforms for collaboration on process/device/circuits, visualization/quantification of manufacturing effects at the mask layout level, and fast/approximate physical modeling for first-cut design decisions. The examples have evolved from research supported over the last several years by DARPA, SRC, Industry and the U.C. Discovery Program on aberrations, illumination, polarization, CMP, plasma etching and device variation. DFM tools must enable complexity management with very fast approximate models across process, device and circuit performance with new modes of collaboration. Circuit Designers have good complexity management skills can add value by participating in this collaboration. Collaborations can be promoted by supporting multiple views of the trade-offs in terms of the natural intuitive parameters of each collaborator. Many of the nonidealities of manufacturing can be expressed at the mask plane in terms of lateral impact functions. This allows visualization and quantitative assessment of effects that are not easily captured even with large sets of design rules. Pattern Matching and Perturbation Formulation have promising exceptional speed and adequate accuracy for implementing these lateral impact assessments.

11:00am **PS2+MS-MoM10 Feature Profile Simulation for Organic Low-k Etching in 2f-CCP in $H_2/N_2$**, ***T.Y. Yagisawa***, *T. Makabe*, Keio University, Japan

As the size of ULSI continuously shrinks up to 45 nm in 2010 and multi-layer interconnect with more than 12 layers is applied, RC (resistance-capacitance) signal delay should be made smaller to meet the demand for higher performance of signal transmission. The dielectric constant of interlayer dielectric (ILD) can be reduced by lowering electric polarizability of the material. Alternatively introducing nano-holes within the material to reduce its density, decreases the k value. Increasing porosity is considered as a promising candidate for obtaining low-k ILD, though it may bring up new serious problems in its processing. Materials with low dielectric constant tend to possess poor mechanical strength and adhesiveness to the wire. In addition, low-k dielectric has low heat conductance and low resistance against heat, which makes it difficult to go through the post annealing in back-end processes. Currently, $H_2/N_2$ plasma is developed as the most suitable tool for the etching of organic low-k material. The etching profile is determined under the balance among isotropic etching by reactive H radical, physical sputtering by energetic ions and surface protection by the deposition of N radical. In order to attain the optimal profile, detailed understanding of these elements throughout the whole plasma etcher is strongly required. We have developed an integrated simulation consisting of the flux-velocity distribution of reactive species and the feature profile evolution of organic low-k etching in two frequency capacitively coupled plasma (2f-CCP) in the admixture of $H_2/N_2$.[1] In the present study, we will first estimate the density of reactive species, such as H, N and $NH_x$ radicals, generated mainly via direct dissociation from parent gas molecules. Further, the effect of dissociation degree on the etching profile will be discussed as a function of the mixture ratio of feed gases.

[1]K. Ishihara et. al., Plasma Physics and Controlled Fusion, 48, B99 (2006).

11:20am **PS2+MS-MoM11 Removal of Scallops formed during Deep Via Etching for 3D Interconnects**, ***Y.-D. Lim***, *S.-H Lee, C.-H. Ra, W.J. Yoo*, Sunkyunkwan University, Korea

Three dimensional (3D) integration using chip-to-chip interconnects is currently receiving great attention since it can bring about substantial advantages in high packing density, low power consumption and high speed operation over planar circuits integration. Deep etching of high aspect ratio vias is known be the most critical step to realize the 3D interconnects. When the Bosch process which alternately introduces SF6 for isotropic etching and C4F8 for sidewall passivation is implemented to form deep via holes, the formation of scallops along the sidewall is unavoidable and poses a serious obstacle to scale down design rule in this scheme. In this work, we investigated methods to remove scallops using post O2 based plasma treatment assisted by subsequent HF based wet etching treatment, when inductively-coupled plasma etching had been applied to form various via hole sizes down to 2.5um with depths up to 100um. According to the experimental results, the removal of scallops was dependent on the via hole size, the orientation of scallop directed out of the sidewall, the combination of the post plasma etching chemistry and the subsequent wet etching chemistry, and the profile of etched structure. Furthermore, it was found that the removal of scallops is more effective for vias of larger and for more vertical structures. The technology developed in this work was proven to be suitable for subsequent electroplating of Cu interconnects.

11:40am **PS2+MS-MoM12 High-rate Deep Anisotropic Silicon Etching with the Expanding Thermal Plasma Technique**, ***M.C.M. van de Sanden***, *M.A. Blauw,* Eindhoven University of Technology, Netherlands, *F. Roozeboom,* NXP Semiconductors Research, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Emerging microsystem and 3D interconnect technologies require high anisotropic etch rates to accommodate Si etch depths exceeding 200-300 µm and aspect ratios higher than 10. Using inductively coupled plasma (ICP) reactors there has been a steady improvement of the performance of deep anisotropic Si etching, however, it is unclear whether sufficiently high etch rates can be obtained by continuous innovation of the existing ICP technology. Following our work on high-rate deposition of a wide variety of materials, we have explored deep anisotropic Si etching with the expanding thermal plasma (ETP) technique using fluorine-based chemistries. The ETP technique consists of a remote high-density plasma source and due to a low downstream electron temperature (< 0.3 eV) it has a good control of the plasma chemistry and ion energy. Both a cryogenic etching process and a time-multiplexed etching process were developed using $SF_6$-$O_2$ and $SF_6$-$C_4F_8$ etch chemistries, respectively. The ion energy was controlled by employing several substrate biasing schemes, including rf and pulse-shape biasing. In this contribution we will present data on etch rates, anisotropy, and selectivity with regard to the hard mask and it will be demonstrated that etch rates up to 12 µm/min and selectivities higher than 300 can be obtained by the ETP technique. Insight in feature profile control will also be presented and it will be shown that feature profiles are comparable to those obtained with ICP reactors. This novel, ETP-based deep anisotropic silicon etching technique might therefore be an attractive alternative for the fabrication of silicon microstructures with high-aspect-ratio features.

**Plasma Science and Technology**

**Room: 607 - Session PS-MoA**

**Plasma Processing for High k, III-V and Smart Materials**

**Moderator:** L. Stafford, University of Houston

2:00pm **PS-MoA1 Activation Energies for $HfO_2$ and Si Etching in $BCl_3$ Plasmas, and Boron Cleaning from Si in $H_2$ Plasmas**, ***C. Wang***, *V.M. Donnelly*, University of Houston

We have investigated plasma etching of a high dielectric constant material, $HfO_2$, as well as poly-Si in $BCl_3$ plasmas. Etching rates of $HfO_2$ and poly-Si were studied as a function of substrate temperature ($T_s$) and plasma source power, and activation energies for $HfO_2$ and poly-Si etching were measured at several powers. There is only a slight increase in the etching rate of $HfO_2$ and poly-Si with increasing temperature. Activation energies range from 0.2 to 0.9 kcal/mole for $HfO_2$ and 0.8 to 1.8 kcal/mole for Si, with no obvious dependence on source powers over the range studied (20 to 200 W). These low activation energies suggest an etching mechanism in which product removal is limited by chemical sputtering of the chemisorbed layer on the surface and higher $T_s$ modestly increases the reaction rate during the ion "thermal" spikes. $H_2$ plasma cleaning of the thin B-containing layer remaining after $BCl_3$ plasma etching of $HfO_2$ on Si was also studied. Previously, we have reported that B can be cleaned from Si in dilute $H_2$/Ar (1% $H_2$) plasmas in 20 s at room temperature, provided the reactor chamber was cleaned in pure $H_2$ plasmas first with sample absent. Here we present a study of boron cleaning in dilute $H_2$/Ar plasmas at elevated substrate temperatures, using x-ray photoelectron spectroscopy to measure B removal rates for individual $BCl_xO_y$ moities. We have found that the B cleaning rate is faster at higher $T_s$. An activation energy of 2.7 kcal/mole was obtained for total B removal in a 1% $H_2$/Ar plasma. Conversely, the Si etching rate under these conditions displayed little if any dependence on substrate temperature; the activation energy was between 0.2 and -0.6 kcal/mole. Therefore, it is advantageous to remove B at higher $T_s$ to minimize Si removal. For example, at $T_s$ = 235 °C, ~90% of B is cleaned from Si in less than 10 s, while <10 Å of Si is removed in this period. Moreover, it was found that etching of Si stops and a Si-oxide layer forms if oxygen is present in the $H_2$ plasma (e.g. from erosion of silica components in the reactor). Consequently, still higher selectivities of B removal with respect to Si are possible under conditions where a small amount of oxygen is present in the $H_2$/Ar plasma.

2:20pm **PS-MoA2 Analyses of Deposition/Etching Regimes during Selective Etching of $HfO_2$ on Silicon in $BCl_3$ Plasmas: Impact of Chamber Walls**, ***E. Sungauer***, ST Microelectronics, France, *X. Mellhaoui, E. Pargon,* LTM/CNRS, France, *Th. Lill,* Applied Materials Inc., *O. Joubert*, LTM/CNRS, France

With the continuous scaling down of CMOS devices to ensure higher speed and density, the thickness of the $SiO_2$ gate dielectric is expected to be reduced down to 1nm for the 45 and 32nm technological nodes. This thickness reduction brings some serious issues such as increased gate leakage current and reduced oxide reliability. Therefore, high-k metal oxides, and more particularly $HfO_2$ have been considered as alternative materials to provide substantially thicker dielectric layers for reduced leakage current and increased gate capacitance. The present work focuses on the understanding of $HfO_2$, $SiO_2$ and Si etching mechanisms in $BCl_3$ based plasmas. $BCl_3$ seems to be a promising gas providing high etch selectivity between $HfO_2$ and Si substrates. The 200mm wafers are etched in an industrial ICP reactor, and then transferred under vacuum into an X-ray Photoelectron Spectroscopy (XPS) analysis chamber to investigate surface modifications induced by plasma exposure. XPS experiments help us in understanding the mechanism driving the etch selectivity between $HfO_2$ and Si-containing substrates. The role of Boron is fundamental since Boron by reacting with Silicon and forming Si-B bonds favour the growth of $BCl_x$ polymer on Silicon surfaces slowing down Silicon etching. On the other hand, on $HfO_2$ surfaces Boron is directly involved in the etching by helping the formation of volatile BOCl etch products. The ionic bombardment plays also a key role since it controls the BCl deposition rate. The ion energy threshold which controls the transition between etching and deposition is lower on $HfO_2$ than on Si and $SiO_2$ wafers, implying that infinite etch selectivity between $HfO_2$ and Silicon can be obtained if the ion energy is well adjusted. In-situ kinetic ellipsometric measurements were also carried out on $HfO_2$, $SiO_2$ and Si substrates to monitor in real time the etching/deposition transition during $BCl_3$ plasma exposure. These experiments have revealed that the etch or deposition rate is linear with time only after a transient regime of about 10s and that during the10 first seconds, $HfO_2$, Silicon and $SiO_2$ show very different kinetic behaviors. We also observed that reactor wall conditioning plays a key role in controlling $BCl_x$ deposition on the wafer and that infinite selectivity can be obtained by coating the reactor walls with carbon layer prior etching in $BCl_3$.

2:40pm **PS-MoA3 Optical Emission Study of an Inductively Coupled $Cl_2/H_2$ Plasma during InP Etching of Micro-nanostructures used for Photonic Applications**, ***L. Gatilova***, *S. Bouchoule, S. Guilet,* Laboratoire de Photonique et de Nanostructures (LPN)-CNRS, France, *P. Chabert*, Laboratoire de Physique et de Technologie de Plasmas (LPTP)-CNRS, France

Cl2/H2-based chemistry has proven to be very efficient for highly anisotropic ICP etching of InP-based heterostructures used in photonic devices. It was shown recently that the Cl2/H2 ratio is a key parameter to control the sidewall profile. At low pressure (0.5mT-1mT), the onset of anisotropic regime occurs at H2 = 35-45%, where the evolution of the etch rate with H2 percentage shows a maximum. A possible explanation, proposed in literature, is the decrease of the reactive atoms and ions (Cl, Cl+) because of the by-products (i.e. HCl) formation. However, deeper understanding of InP etching mechanism requires more detailed investigations. We have used OES combined with electron and positive ion density measurements, during the etching of InP ridge structures, to obtain insight into the etch mechanism of InP in Cl2/H2 ICP plasma. The pressure was 0.5 mT, the ICP power was 800W, the DC bias voltage was –150 V, the total gas flow was kept constant at 28 sccm, and the H2 concentration is varied from 0 to 100%. The main emission lines recorded during the etching process were Cl (725.7 and 754.7nm), H (656.3nm), In (325.6, 410.2, 451.1nm), InCl (350nm), PH (340nm). In order to estimate the relative atom concentrations, 10% of argon was added in the initial gas mixture. The etch rate and the In-line intensity have roughly the same behavior versus Cl2/H2 ratio, which can be divided into three regions. For H2 concentration between 0-25% (corresponding to strongly undercut profiles), the etch rate rapidly decreases with %H2 increase, so as the positive ion current and the reactive species concentration – the Cl density falls down continuously when H2 increase from 0 to 100%. For H2 concentration greater than 60%, the etch rate also decreases down to very low values < 100nm/min and the etched surface becomes grassy. Despite the H2 concentration increases, the concentration of H atoms decreases, probably due to the decrease in the electron density. For intermediate H2 concentration (the second region which lies between 35% and 45%), corresponding to the highly anisotropic region, the etch rate remains constant. This intermediate region corresponds to a maximum in H concentration. The etch rate could thus be the result of a balanced effect between the Cl density decrease and the H density increase, with a change in etching mechanisms of P-atoms; for high H density P-atoms leave the InP surface by PHx formation, as suggested by the increase of PH-line intensity.

3:00pm **PS-MoA4 Dry Etching of $Ge_2Sb_2Te_5$ for Phase Change Memory Applications: Characterization and Design of Low Damage Process**, ***P. Petruzza***, STMicroelectronics Italy

In order to realize highly integrated PRAM involving $Ge_2Sb_2Te_5$ (GST) thin films,[1] the etching process must be developed. Until now, there were several work devoted to the investigations of etching properties of GST films using fluorine and chlorine based plasma chemistries.[2] Unfortunately, the relationships between plasma parameters and damage of GST thin films remained out of attention. We investigated the etching behaviours of GST in terms of etching process parameters such as pressure, gas, temperature, gas flux directionality in closely bound up with film stack of GST and subsequent problems such as voiding, poisoning of GST ad decreased mechanical strength. Etching of chalcogenide alloy may result in chemical and structural modification of the sidewall and surface residues. GST reactive ion etching plasmas have been studied by measuring etch rate and composition using XRF spectroscopy, etch profile, surface - chemical aspects and bulk morphology by employing TEM/SEM. Etching experiments were performed in a low pressure inductively coupled plasma reactor supplied with 13.56 MHz rf powers. GST thin films were prepared on SIN substrate. Damage and degradation of GST has been investigated by down stream plasma treatments after GST etching definition. SEM cross section analysis shows that the sidewalls of GST are eroded after ashing process. The thickness of damaged thin layer depends of etching chemistry and of other process parameters such as temperature. In the present work it's explained the results obtained with this method for different etching gas chemistry of chalcogenide alloy. The experiments results show that $Cl_2$ etching process have induced a composition change of the alloy and thick erosion in sidewalls of GST film patterns. Unlike $Cl_2$, fluorine chemistry

avoids GST erosion. In order to perform manufacturability phase change memory: using the obtained results, a etching process by $Cl_2$ free chemistry with suitable process parameters has been provided.

[1] F. Pellizer, A Pirovano, et all., Proc. Symposiumon VSI technology, june 2004, pg 18-19.
[2] Sung-Min Yoon et al., Japanese Journal of Applied Phisics, Vol. 44, No 27, 2005, pp L 869-L 872 .

3:40pm **PS-MoA6 John A. Thornton Memorial Award Lecture - Etching of SiC, GaN and ZnO for Wide Bandgap Semiconductor Device Applications**, ***S.J. Pearton****, *L.F. Voss, W.T. Lim,* University of Florida*, R.J. Shul*, Sandia National Laboratories **INVITED**

A review will be given of dry etching of three technologically important wide bandgap semiconductors, namely GaN,SiC and ZnO. Dry etching of GaN is needed for mesa formation on electronic and photonic devices and for through-wafer vias on power devices. Generally chlorine-based plasma chemistries are used, with etch rates in the range of a few thousand angstroms per minute to almost one micron per minute. A typical issue is the preferential loss of nitrogen from the near-surface region, leading to the presence of an n-type surface layer after etching. This can be used to advantage in improving contact resistance of n-type Ohmic contacts. For SiC, the main chemistries are based on fluorine and changes to the surface electrical properties are less of an issue. For ZnO, the low volatility of all Zn etch products leads to low etch rates at room temperature and changing to iodine or bromine chemistries does not improve the removal rates. Examples will be given of device etching processes for all three materials systems.

4:20pm **PS-MoA8 Comparative Study of ECR and ICP Plasma Etching of High-k Dielectric $HfO_2$ Films with $BCl_3$-Containing Gas Chemistries**, ***D. Hamada****, *K. Nakamura, Y. Ueda, M. Yoshida, K. Eriguchi, K. Ono*, Kyoto University, Japan

Etching of high-k materials is indispensable for their removal in integrating them into device fabrication. Moreover, the high-k etching is required for chamber cleaning of the deposition apparatuses in mass production. This paper presents a comparative study of the etching of high-k $HfO_2$ films in electron cyclotron resonance (ECR) plasma and inductively coupled plasma (ICP) reactors with $BCl_3$-containing chemistries, where emphasis is placed on a better understanding on the etching mechanisms concerned. The ECR reactor had a configuration of divergent magnetic fields, and the discharge was established by 2.45-GHz microwave powers of 600 W. The ICP reactor had a three-turn planar coil, and the discharge was established by 13.56 MHz rf powers of 300 W. Feedstock gases were $BCl_3$, $Cl_2$, $O_2$, and Ar at total pressures of 2-20 mTorr with a total flow rate of 40 sccm. The significant differences between ECR and ICP plasmas are: the etching of $HfO_2$ without rf biasing was obtained in ECR $BCl_3$-containing plasmas, while was not obtained in ICP; moreover, the etch selectivity $HfO_2$/Si was >> 1 with no bias in ECR, while was < 1 with bias in ICP. In ECR, the $HfO_2$ etch rate was increased in order of $BCl_3$, $BCl_3/O_2$, $BCl_3/Cl_2$, and $BCl_3/Cl_2/O_2$; typically, the $HfO_2$ etch rate in $BCl_3/Cl_2$ was ~100 nm/min at ~60% $Cl_2$ with a selectivity of ~10 over Si, and a high selectivity >50 was obtained at 40-50% $Cl_2$ with a $HfO_2$ etch rate of ~50 nm/min. The Langmuir probe measurements indicated that in ECR, the difference between the plasma and floating potentials was of the order of 10 V, which is lower than the threshold ion energy ~26 eV known for the $HfO_2$ etching in $BCl_3$ plasmas. In contrast, the $HfO_2$ etching in ICP occurred with additional rf biasing, where the threshold energy was estimated to be ~ 30 eV from the difference between the plasma potential and dc self-bias voltage; the etch rate increased with increasing rf bias power, being ~50 nm/min with a $HfO_2$/Si selectivity of ~0.5 at an ion energy of ~100 eV in $BCl_3/Cl_2$. The gas-phase and surface chemistries responsible for the $HfO_2$ etching is discussed based on several plasmas and surface diagnostics including OES, QMS, LIF, FTIR, and XPS, to achieve higher etch rate and selectivity under conditions of low ion energies and/or less ions.

4:40pm **PS-MoA9 Investigation of Surface Reactions for Chlorine-Based Plasma Etching of Nitrided Hafnium Silicates**, *R.M. Martin,* University of California at Los Angeles*, B. Xia, A. Misra,* Air Liquide*, **J.P. Chang***, University of California at Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-45nm 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 $SiO_2$ and $HfO_2$ was first studied in $Cl_2$ and $BCl_3$ plasmas, to allow for studies of the etching of HfSiON with well controlled and varying compositions of Si and N in $HfO_2$. The etch rates of nitrided hafnium silicates were found to increase with the square root of ion energy, and the etching rate of films increased with increasing nitrogen incorporation as well as $SiO_2$ percentage in the film. 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 $HfO_2$, suggesting that Si and N incorporation modifies film structure/density. In addition, nitrogen was detected removed in the form of $SiN_2Cl_x$, and more nitrogen remains on the surface of the Hf-rich films than the Si-rich films. This suggests that the removal of N is related to its bonding within the film. Hafnium and silicon were removed as $HfCl_x$, $SiCl_x$, and $SiO_2Cl_x$, and increased with ion energy. A generalized phenomenological model will be presented to describe the effect of $SiO_2$ and N incorporation on the etching behavior of $HfO_2$.

5:00pm **PS-MoA10 Plasma Source-Dependent Charging Damage Polarities in the Performance Degradation of MOSFETs with Hf-based High-k Gate Dielectrics**, ***M. Kamei****, *K. Eriguchi, H. Fukumoto, K. Ono*, Kyoto University, Japan

We report that the polarities of charging damage in n- and p-ch MOSFETs with Hf-based high-k gate stack ($HfAlOx/SiO_2$) depends on plasma sources, in contrast to those with conventional $SiO_2$. In order to investigate the charging polarity in MOSFETs with the high-k gate stack (high-k) and those with $SiO_2$ ($SiO_2$), the gate leakage current, drain current - gate voltage, and capacitance - voltage measurements were conducted for at least 12 difference devices with different device sizes (antenna ratio) to evaluate the deviation. The electrical thicknesses by capacitance-voltage measurements are ~2.7 and ~7.4 nm for high-k and $SiO_2$, respectively, while both devices have approximately the same physical thickness of 7 nm. ECR with the bias power of 200 W under two plasma conditions, Ar- and Cl-based gas mixtures, were utilized to induce the charging damage. The Langmuir probe and bias voltage measurements were carried out for correlating the electrical data to plasma parameters to understand the mechanisms. For Ar-plasma, high-k gate stacks were identified to suffer from negative charge trapping for both n- and p-MOSFETs, while $SiO_2$, from positive charge trapping for pMOSFET. For Cl-plasma on the other, positive charge trapping was observed for n- and p-MOSFETs with high-k, in contrast to Ar-plasma. The observed unique features in high-k were attributed to the difference in the measured ion currents and electron densities between Ar and Cl plasmas as well as the effects of device polarities (n-/p-ch) and asymmetric energy band structures of high-k gate stacks on the stress configurations during plasma exposures. It is suggested that Ar- and Cl-plasmas exhibit different current sources (positive, negative, or bi-directional current sources) in response to device structures, in particular with high-k subject to charge trapping. In addition to the experimental result that high-k devices are more susceptible to plasma charging damage compared to $SiO_2$ devices, it can be concluded that the observed plasma source-dependent charging polarity for high-k devices, in particular pMOS, should be considered in future device design rules and plasma process designs.

## Advanced Surface Engineering

## Room: 617 - Session SE+PS-MoA

## Pulsed Plasmas in Surface Engineering

**Moderator:** J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-MoA1 Modulated Pulse Power Deposition of Nanometer-Scale Multilayered Coatings**, *R. Chistyakov, B. Abraham,* Zond, Inc./Zpulser, LLC*, **W.D. Sproul***, Reactive Sputtering, Inc.*, J.J. Moore, J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations directly affect the degree of ionization of the sputtered material. In this study, the MPP plasma generator was controlled by a special electronic device that allowed the generation of two different plasma discharges within the same deposition cycle. Nanometer scale layers of material deposited under the two different plasma condition were alternately deposited, and the thickness and structure of each nanolayer was controlled by varying the output voltage pulse shape of the

***** John A. Thornton Memorial Award Winner

MPP plasma generator. Films of carbon and reactively deposited titanium nitride and chromium nitride were sputtered, and the film structure, orientation, and mechanical properties were analyzed and measured. These variations in the plasma conditions directly affect the film properties, and results of the film property measurements will be presented.

2:20pm **SE+PS-MoA2 Reactive High Power Impulse Magnetron Sputter Deposition of Alumina**, *E. Wallin, S. Swedin, M. Lattemann,* ***U. Helmersson***, Linköping University, Sweden

Alumina, $Al_2O_3$, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. In the present work, alumina thin films have been deposited using high power impulse magnetron sputtering (HIPIMS) of an Al target in $Ar/O_2$ gas mixtures. HIPIMS is a new and promising technique for ionized physical vapor deposition (I-PVD), in which a high degree of ionization of the deposition flux as well as an inherently high energy of the depositing species can be achieved at relatively low average power, by applying high power pulses with a low duty factor (typically around 1 %) to a conventional sputtering target (see, e.g., Helmersson et al., Thin Solid Films 513, 1 (2006)). Stoichiometric alumina films could be grown in a stable and essentially arc free process at rates which are high compared to the deposition rate for pure Al metal and comparable to, or even higher than, what can be achieved with traditional DC deposition methods. A model qualitatively describing and giving explanations for this behavior of the reactive process will be presented. The resulting films were investigated by x-ray diffraction, as well as scanning and transmission electron microscopy. Films deposited directly onto Si substrates at a substrate temperature of 400 °C were found to have a microstructure consisting of small, equiaxed grains with a diameter of the order of 10 nm, and with γ-alumina as the only detectable crystalline polymorph. The results demonstrate the potential of depositing dielectric films at relatively high rates using HIPIMS. In addition, HIPIMS deposition of such films opens the possibility of utilizing the ionized deposition flux to improve the film quality and affect the structure of the coatings, also at reduced substrate temperatures.

2:40pm **SE+PS-MoA3 Effect of Sub-Surface Reactions on the Growth of Nano-Structured Functional Thin Films Deposited under Energetic Ion Bombardment**, *A. Amassian, M. Dudek, P. Jedrzejowski, R. Vernhes, O. Zabeida, P. Desjardins, J.E. Klemberg-Sapieha,* ***L. Martinu***, Ecole Polytechnique, Canada **INVITED**

Recent advances in science and technology stimulate the development of new coating materials, surface and interface engineering processes and thin film systems that provide an ever increasing performance in numerous areas ranging from optical and optoelectronic to aerospace, automotive, biomedical, microelectronic, and other applications. Many successful solutions in these particular fields have been identified when using ion-assisted deposition of thin films and thin film systems with tailored functional characteristics including the complex refractive index, the mechanical properties such as stress, hardness, friction coefficient and wear, the electrical conductivity, the gas and vapour permeation, and many others. In this context, we have recently investigated ion-surface interactions in a plasma environment (biased-controlled PECVD and PVD) using a methodology combining in situ real-time spectroscopic ellipsometry (RTSE), dynamic Monte-Carlo simulations, and different complementary methods such as ERD, HRTEM, SEM, AFM and others. These have the capability to detect and simulate subplantation-related processes, such as sub-surface structural and compositional modifications, and interface broadening, on time and depth scales relevant to functional coatings deposition. The ion-induced effects result in (i) rapid structural (<< 1 s) and compositional (< 2 s) changes as deep as ?10 nm below film or substrate surfaces, as well as (ii) significant ion mixing and interface broadening, and (iii) relocation of a large proportion of deposited atoms below the growth surface. Specifically, following a description of the principal physical processes, we will show examples when the above-mentioned methodology helped to enhance our understanding of the film growth and interface evolution for numerous single and multilayer functional coatings comprising TiO2, SiO2, Si3N4, ITO and the nanocomposite superhard TiN/SiN and TiCN/SiCN systems. We will also discuss the ion-controlled growth mechanisms in the context of new deposition approaches such as plasma pulsing.

3:40pm **SE+PS-MoA6 Microstructure Evolution in High Power Magnetron Sputter Deposited Titanium Nitride**, ***M. Lattemann***, *D. Jädernäs, U. Helmersson*, Linköping University, Sweden

Transition metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, high temperature stability, low resistivity, and good optical properties. As a result they have become of high technological and scientific importance and are used in a wide range of applications. NaCl δ-TiN has received by far the most attention and is therefore often used as a model system. In this work, TiN thin films were deposited onto MgO(100) and MgO(111) substrates in an $Ar/N_2$ atmosphere using high power impulse magnetron sputtering (HIPIMS). HIPIMS has earlier been proven to produce a highly ionized metal flux exhibiting a broad ion energy distribution with energies up to 100 eV advancing surface processes. It was shown that these ion energies are sufficient to produce fully dense films even at ambient temperature. However, the high amount of metal species with an energy around 1 eV promote the formation of underdense grain boundaries as the energy only allows the ions to interact with the nearest neighbor sites by single hop events. At ambient temperature and grounded substrate, the TiN thin films show a columnar structure with almost random orientation of the crystals as a result of combination of arriving species with high and low mobility as well as highly energetic ions creating defects and nucleation sites. The window for epitaxial growth of TiN for a variety of different process parameters was investigated. E.g. a more monoenergetic ion energy distribution can be achieved by tailoring the substrate bias and process conditions. In addition to the metal ion energy and substrate temperature, also the effect of assisting gas ion irradiation was investigated both during the pulse and in between the pulses, where no deposition occurred. In this way, the onset and breakdown of structure relation towards polycrystalline morphology can be monitored. The resulting structure of the TiN thin films was investigated by x-ray diffraction and high resolution transmission electron microscopy.

4:00pm **SE+PS-MoA7 High Power Impulse Magnetron Sputtering (HIPIMS): Scaling Up to the Industrial Level**, ***G. Greczynski***, *J. Bohlmark*, Chemfilt Ionsputtering AB, Sweden

High Power Pulsed Magnetron Sputtering (HIPIMS or HPPMS) is a novel magnetron sputtering technique that draws increasing interest due to the ability to form the droplet-free films out of highly ionized vapor of the target material. Invented by Kouznetsov in 1999 (US patent US6296742) HIPIMS has gone the long way and is nowadays entering the stage of commercial applications. The focus of the work presented here is the basic parameter study performed on the industrial system equipped with HIPIMS power supply capable of delivering up to 10 kW average power in MW pulses. The target material used is Ti/Al and Ti. Purely metallic films, as well as, reactively sputtered TiAlN and TiN films were grown. The deposition rate and film quality were studied as a function of the energy per pulse (up to 20J), pulsing frequency (up to 500Hz), working gas pressure and the substrate bias. The degree of ionization, that was simultaneously monitored with optical emission, reached 90% under optimum conditions. Results are compared to the films produced with the state-of-the-art industrial DC coater. It is apparent from this study that the technique can be successfully used in the industrial applications.

4:20pm **SE+PS-MoA8 Mechanisms of Adhesion Enhancement by High Power Impulse Magnetron Sputtering**, ***A.P. Ehiasarian***, Sheffield Hallam University, UK **INVITED**

Adhesion to steel and carbide substrates is one of the primary factors determining coating performance under environmental attack such as wear in cutting and automotive engine operations, errosion-corrosion, and high temperature oxidation. Technologies that improve adhesion aim to sputter-clean the substrate by high energy ion bombardment with energy >500 eV. These energies are sufficient for ions to be implanted into the bulk of the substrate to a depth of several monolayers (1-3 nm). Therefore the chemical composition of the bombarding flux can have a strong influence on the structure of the coating-substrate interface. Technologies that use gas ion bombardment typically incorporate Ar as interstitial or at vacancy sites generated in the steel or carbide lattice by the high energy of irradiation. The inert nature of Ar means that it does not form bonds with the surrounding atoms and thus greatly disturbs atomic ordering and increases stress. In the case of high power impulse magnetron sputtering (HIPIMS) plasmas operating at peak current of 2 $Acm^{-2}$, the ion bombardment flux contains high fractions of metal ions. For HIPIMS of Cr and Ti, the ratio $Ar^{1+} : Me^{1+} = 1 : 1$ was observed with energy-resolved mass spectroscopy, whilst the metal ion-to-neutral ratio was $Me^{1+} : Me^{0} = 1 : 1$ as determined from atomic absorption spectroscopy. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) analysis of 304 stainless steel bombarded at 600 V by HIPIMS of Cr showed a layer of implanted Cr ions with depth of 5-8 nm, resulting from ballistic implantation as confirmed with TriDyn simulations. High-resolution TEM revealed that this region is highly crystalline with low defect density, probably due to the substitutional incorporation of Cr ions in the steel lattice. Incorporation and retention of Cr is improved by irradiation- and temperature- enhanced diffusion. As a result of the crystalline interface, the coating nucleated in local epitaxial growth mode which was maintained over several microns in lateral direction. A number of susbtrate-coating combinations demonstrated such epitaxy, for example for steel substrates: CrAlN, CrN, VN, TiAlN, and for γ-TiAl substrates - CrAlN, and CrN. This

resulted in significant improvements to the adhesion and performance in wear and cutting of Ti and Al tests.

5:00pm **SE+PS-MoA10 Deposition Rate of High Power Pulsed Magnetron Sputtered Cu**, ***J. Emmerlich***, *S. Mráz, R. Snyders, K. Jiang, J.M. Schneider*, RWTH Aachen University, Germany

In high power pulsed magnetron sputtering (HPPMS), several kW target power are dissipated during µs pulses resulting in a high degree of ionization of the sputtering gas as well as the sputtered target material.[1] A major drawback of this deposition process is reported to be the low deposition rate compared to d.c. magnetron sputtering (dcMS). Self-sputtering, due to a metal-ion dominated plasma later in the pulse, and plasma conductivity may play a large role in the deposition rate loss. However, the high target potential (up to ~2kV) applied during HPPMS influences the sputtering yield induced by both, the sputtering gas and the target ions (self-sputtering). The effect of the energy dependent sputtering yield on the deposition rate is discussed for Cu. Using transport-of-ions-in-matter (TRIM) software, we simulated the sputtering yield for a Cu target bombarded with energetic $Ar^+$ and $Cu^+$ ions for dcMS and HPPMS target potentials. The results show that the deposition rate of HPPMS compared to dcMS based on an energy dependent sputtering yield is in the range of 77% to 43%.

[1]K. Macák, V. Kouznetsov, J. Schneider, and U. Helmersson, J. Vac. Sci. Technol. A 18, 1533 (2000).

**Plasma Science and Technology**

**Room: 606 - Session PS1+TF-TuM**

## Plasma Enhanced Atomic Layer Deposition and Plasma Deposition

**Moderator:** S. Agarwal, Colorado School of Mines

8:00am **PS1+TF-TuM1 Characteristics for $HfO_2$ Gate Dielectrics Deposited by Remote Plasma ALD Method**, *S. Kim, **H. Jeon***, Hanyang University, South Korea **INVITED**

Many high-k dielectric materials have been studied extensively to replace current gate dielectric materials such as $SiO_2$ and $SiO_xN_y$. Among the high-k dielectric materials, Hf-oxide is considered to be one of best choices for 45 nm technology and beyond. However, most of high-k oxides such as $HfO_2$, $ZrO_2$, $Ta_2O_3$, and $TiO_2$ are transition metal oxides with the ionic nature and have poor interface quality and poor thermal stability with Si substrate. In addition, they exhibits high oxide traps and interface state densities, and large amount of oxygen vacancies, and are easily crystallized compared to $SiO_2$. To overcome these drawbacks of high-k oxides, the technologies for growing high quality high-k oxides and improving the interface properties between high-k oxide and Si substrate are required. In this study, we chose $HfO_2$ as high-k gate dielectrics and atomic layer deposition (ALD) as a deposition method. Among many deposition methods, ALD method is studied by many researchers because of its thin film deposition superiority. In our lab we applied both direct plasma ALD (DPALD) and remote plasma ALD (RPALD) methods to grow $HfO_2$ thin films on Si substrates. These two different plasma methods exhibited the different thicknesses of silicate interlayer. We believe this interlayer is critical for the degradation of high-k dielectric materials. To investigate these interlayers we grew several different buffer layers before $HfO_2$ growth. These buffer layers were formed by remote plasma oxidation (RPO) and nitridation (RPN) on Si substrates to monitor this interlayer, to suppress the initial formation of Hf silicate or interlayer and to improve the interlayer quality. The buffer layers were thin $SiO_2$, $SiO_xN_y$, $Al_2O_3$, nitrided Al silicate and nitrided Hf silicate layers. The $HfO_2$ films with buffer layers suppressed silicate formation or growth of an interlayer more effectively than those without buffer layers. The $HfO_2$ films with buffer layers also showed lower effective oxide thickness (EOT), lower effective fixed oxide charge density ($Q_{f,eff}$), and lower leakage current density compared to those without buffer layers. The physical and electrical properties of $HfO_2$ with buffer layers will be presented and discussed depending on the various buffer layers.

8:40am **PS1+TF-TuM3 Pulsed Plasma-Enhanced Pulsed CVD of $Y_2O_3$ in MIM Capacitors**, ***C, Vallee***, *M. Kahn, E. Gourvest, M. Bonvalot, O. Joubert*, CNRS, France

The development of integrated metal-insulator-metal (MIM) capacitors for advanced analog and rf circuits aims at achieving development of capacitors with higher capacitance density, low leakage current, and good voltage linearity. High k materials are thus integrated and evaluated as MIM dielectrics. Moreover, system-on-chip (SOC) applications also require a deposition process with a low thermal budget which can be carried out with a plasma deposition process. In the past, we have shown interesting results on MIM capacitors based on $Y_2O_3$ materials deposited by a low temperature process, namely pulsed liquid injection MOCVD assisted or not by a capacitive RF plasma. With the plasma, depositions have been achieved at temperatures as low as 300°C, and for this reason, good results have been obtained with TiN as bottom electrode. Without plasma, the deposition takes place at 450°C and a non desirable $TiO_x$ interface is formed, which degrades the MIM electrical properties. In this study, we compare $Y_2O_3$ MIM capacitors deposited on $WSi_{2.3}$ substrates when assisting the pulsed CVD process by a pulsed RF plasma instead of a continuous plasma. With $WSi_{2.3}$ substrates, the interfacial layer is $SiO_2$-like, which can be beneficial to the MIM electrical properties in terms of linearity behavior. The plasma is pulsed either in phase or out of phase with the pulsed liquid injection of precursors. Moreover, depending on the plasma pulse width and frequency, the plasma can play a role in precursor dissociation and CVD post-deposition in-situ annealing treatment. The electrical behavior C(V) and I(V) of the obtained structures will be presented and discussed in terms of capacitance density, capacitance linearity and leakage currents. They will be correlated to chemical analysis results (XPS and FUV-SE), with special attention devoted to carbon content as well as metal/oxide interface investigations. C(V) curves suggest the presence of positive charges in the oxide, some of which are mobile, when the plasma is continuously applied. In this study, we will show the impact of exposure time of the dielectric to the plasma on the amount of trapped positive charges in the oxide affecting the MIM linearity properties. Moreover, the nature and thickness of the interfacial dielectric layer originate from both oxygen and solvent which can be limited by pulsing the plasma.

9:00am **PS1+TF-TuM4 Engineering Plasma-Enhanced Chemical Vapor Deposition to Deliver Self-Limiting Deposition of Metal Oxide Thin Films**, ***M.T. Seman***, *S. Agarwal,* Colorado School of Mines, *J.J. Robbins,* CMD Research, LLC, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe how conventional plasma-enhanced chemical vapor deposition (PECVD) may be engineered to deliver self-limiting deposition of metal oxides using pulsed power modulation. Self-limiting growth is assured when no deposition occurs during continuous operation with either the plasma on or the plasma off. The requirements that must be met to achieve this behavior are described. The pulsed PECVD technique has the potential to combine the digital control over thickness and composition provided by atomic layer deposition with the high throughput and low temperature capability offered by PECVD. To date the process has been demonstrated for both tantalum[1] and aluminum oxides,[2] and in this paper we focus on the process-property relationships in the former system. Tantalum oxide films were deposited by pulsed PECVD using continuous delivery of oxygen and penta-ethoxy tantalum (PET, $Ta(OC_2H_5)_5$) in a capacitively-coupled reactor. Deposited films were characterized by spectroscopic ellipsometry, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and dielectric performance. The deposition rate per pulse may be readily adjusted over a broad range (1- 10 Å/pulse) using variables such as the PET concentration and the plasma off time. With these variables fixed digital control over film thickness is demonstrated. The process is insensitive to substrate temperature, with a constant deposition rate observed from 90 to 350 °C. Films contain impurities due to carbon and hydroxyl groups, however these signals attenuate as the rate is reduced and are not detectable by FTIR for rates < 3 Å/pulse. Films deposited under these conditions at 190 ºC displayed a high dielectric constant ($\kappa \sim 25$) while maintaining leakage current densities below 1 $\mu A/cm^2$ out to a field strength of 1 MV/cm.

[1] M. Seman, J. J. Robbins, S. Agarwal, and C. A. Wolden, Appl. Phys. Lett. 90, 131504 (2007).
[2] S. Szymanski, M. T. Seman, and C. A. Wolden, Surf. Coat. Technol. in press (2007).

9:20am **PS1+TF-TuM5 Peter Mark Memorial Award Lecture - Plasma-assisted Atomic Layer Deposition: Applications, Opportunities, and Mechanisms**, ***W.M.M. Kessels****, Eindhoven University of Technology, The Netherlands **INVITED**

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with submonolayer growth control. Recently, the extension of the technique with plasma processes is actively being researched. These so-called plasma-assisted ALD processes can provide several potential advantages over thermal ALD for selected applications such as an enhanced growth rate, improved material properties, and lower deposition temperature (down to room temperature). In this contribution, different plasma-assisted ALD configurations such as direct plasma, remote plasma and radical enhanced ALD will be discussed and an overview will be presented of oxide and nitride materials ($Al_2O_3$, $HfO_2$, $TiO_2$, TiN, TaN, etc.) deposited. In particular, remote plasma ALD processes based on halide and metalorganic precursors and plasmas of $H_2$, $N_2$, $O_2$, $NH_3$ and combinations thereof will be described and the resulting material properties will be presented for wide substrate temperature ranges. The versatility of the plasma-assisted ALD process will be illustrated by several applications ranging from the semiconductor industry (capacitor stacks) to emerging applications in the field of 3D-integration in microelectronics (Cu diffusion barriers), photovoltaics (Si surface passivation), energy storage (Li diffusion barriers) and flexible electronics (ultrahigh moisture barrier coatings). Generic insight into the plasma-assisted ALD surface reactions will be presented from mechanistic studies carried out by a variety of in situ techniques: spectroscopic ellipsometry for monitoring film thickness and film properties (including electrical resistivity and crystal phases), transmission infrared spectroscopy to probe reactive surface groups, quartz crystal microbalance measurements to measure surface mass uptake, and mass spectrometry and optical emission spectroscopy to detect reaction products. On the basis of the results, the paradigms for plasma-assisted ALD are reviewed and differences with thermal ALD processes are discussed.

* Peter Mark Memorial Award Winner

10:40am **PS1+TF-TuM9 Silicon Based Coatings by Means of Glow and Townsend Dielectric Barrier Discharges**, ***F. Massines***, CNRS PROMES, France, *N. Gherardi*, LAPLACE CNRS-UPS-INP, France **INVITED**

The development of a PECVD process working at atmospheric pressure and allowing an easy on-line treatment of silicon wafer, glass plate or polymer film is a challenge of great interest. The successful solution will avoid batch treatments and significantly reduce the cost of the coating. The main questions to be solved are how to get a well controlled thin film in terms of chemical composition, structure and thickness? and how to get a high growth rate? Previous to the process development, the main difficulties concern the plasma homogeneity, the gas injection over large dimensions, the control of the atmosphere in the plasma area while the substrate is moving and the efficiency of the transfer of the reactive species to the surface taking into account the very low diffusion of the neutral radicals at atmospheric pressure. In case of two dimensional materials like, dielectric barrier discharge (DBD) appears like the more suitable discharge: it is cold, robust and not disturbed by the movement of the substrate. As example DBD generate the plasma of corona treaters useful for surface activation. However, making a thin film coating having well controlled and uniform properties is more delicate. Homogeneous DBD (HDBD) is a solution to reach that goal. Conditions to get such a HDBD are now widely known and easy to up-scale in one direction allowing to get a uniform plasma band of several meters in the direction perpendicular to that of the substrate movement. This solution is in competition with remote plasmas but knowing that the quenching of excited state drastically increases with the pressure, and as far as the substrate can be moved inside the discharge without inducing perturbation, remote plasma has to be avoid. At atmospheric pressure, the reactive gases leading to the coating formation are diluted in a main gas, which is usually helium, argon or nitrogen. The main gas determines the discharge regime and then the energetic species created during the plasma development. In nitrogen, the HDBD is a Townsend discharge while in noble gases the HDBD is a glow one. In this presentation results concerning SiOx coatings obtained from SiH4 or hexamethyldisiloxane mixed with N2O and diluted in N2 will be compared. The coating thickness, the refractive index and the chemical composition as a function of the gas residence time will be discussed and correlated to the main growth mechanism.

11:20am **PS1+TF-TuM11 Film Microstructure Control and Characterization of Ion Bombardment- Aided Remote Plasma Deposition of Silicon Dioxide Films**, ***M.A. Creatore***, *N.M. Terlinden, M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

The control on thin film growth and microstructure in plasma deposition is a challenging issue. For example, in the case of an inorganic layer on an organic substrate (e.g., $SiO_2$ on polymers), the organic/ inorganic interphase affects the bulk inorganic properties, such as adhesion and moisture permeation barrier performance. Within this framework, ion bombardment-aided remote plasma deposition of $SiO_2$ layers, deposited from a hexamethyldisiloxane/$O_2$ chemistry, is carried out: the purpose is to engineer an interphase allowing the growth of dense, yet adhesive barrier films. This control is achieved by coupling the use of ion bombardment with a graded growth flux, obtained by a gradient (e.g. a decrease) in the hexamethyldisiloxane flow rate during film growth. At constant substrate bias voltage, i.e. constant ion energy, this gradient allows to tune the ion-to-growth flux ratio and the film densification. Initially, an adhesive porous layer is deposited, gradually shifting towards a highly dense barrier layer, due to the increase in the ion-to-growth flux ratio. The role of ion bombardment on the film microstructure is investigated by means of ellipsometric porosimetry, which monitors the refractive index (n) change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity and the pore volume distribution can be extracted. In the absence of ion bombardment porous (n= 1.35-1.38) layers are characterized by an isotherm shape mimicking the structure of disordered mesoporous films (pore diameter in the range of 2-50 nm), i.e. a very broad distribution in pore size and shape, resulting in 20% porosity. A progressive increase in substrate bias voltage leads towards film densification (n=1.46) and induces a change in the isotherm: the adsorption/desorption process becomes reversible since unrestricted ethanol multilayer adsorption occurs on the non- porous surface. When a mild ion bombardment (ion energy of 20 eV) is accompanied by an increasing ion-to-growth flux ratio, both the isotherm and the hysteresis behavior exhibit the transition from meso- to microporosity (pore diameter less than 2 nm). The implications in terms of porosity determination in barrier layers deposited on polymeric substrates will be also addressed.

11:40am **PS1+TF-TuM12 Self-Limiting Growth of Aluminum Oxide by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***S.F. Szymanski***, *M.T. Seman, D. Richards, C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of aluminum oxide by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process the trimethyl aluminum (TMA, $Al(CH_3)_3$) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. Deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy, and dielectric performance. In addition, the plasma and gas-phase chemistry in this system were characterized using optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS), respectively. The chemistry and deposition kinetics were quantified as a function of TMA concentration, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TMA concentration and pulse duration, the depositing rate may be readily adjusted over a broad range (1 - 10 Å/pulse). The deposition rate also decreases with plasma power, and OES is used to highlight the role of atomic oxygen in this process. The chemistry was quantified under steady-state operation using the QMS. It is shown that $O_2$ and TMA are unreactive with the plasma off. In contrast, TMA is completely consumed during plasma operation. Combustion of the TMA precursor is complete, yielding a mixture of CO, $CO_2$, $H_2O$, and $H_2$. Transient experiments show how TMA adsorbed on the walls of the chamber can impact both deposition rate and quality. The deposition rate was found to be independent of temperature for $T_s > 100$ °C. At lower temperatures the deposition rate per pulse increased, but film quality was degraded. Using a combination of ex situ film characterization and in situ diagnostics it is suggested that this behavior may be attributed to thermal chemistry occurring between TMA supplied during the off step with $H_2O$ produced during the plasma on step. This reaction adversely effects film quality, but its effects are mitigated when the both reactor walls and substrate are maintained at temperatures > 100 °C.

12:00pm **PS1+TF-TuM13 Correlation of Surface Reactivity and Gas Phase Properties of CN Active Species in the Plasma Deposition of Carbon Nitride**, ***J. Stillahn***, Colorado State University, *D. Liu*, Dalian Nationalities University, China, *E.R. Fisher*, Colorado State University

Amorphous carbon nitride materials have generated interest due to their potential for commercial applications. One of the possible precursors in the plasma enhanced chemical vapor deposition (PE-CVD) of carbon nitride is the CN radical, but its role in the deposition process is still unclear. In an effort to clarify the processes taking place during film formation, carbon nitride deposition systems have been studied in rf inductively coupled plasmas by utilizing acetonitrile ($CH_3CN$) as a film precursor to allow direct generation of CN active species. The imaging of radicals interacting with surfaces (IRIS) technique has been utilized in our lab to provide a measure of the surface reactivity of the CN radical, R(CN), in these systems. Preliminary results indicate that CN radicals formed in acetonitrile plasmas react with near unit probability during deposition of a-$CN_x$:H films. Results from IRIS studies using other CN precursors will also be discussed. Characterization of gas phase species in these deposition systems has also been performed using spectroscopic and mass spectrometric (MS) methods. MS measurements are consistent with the direct formation of CN active species, and mass spectra are dominated by ions formed by the loss of CN from the parent molecule. Measurement of the relative number density of gas phase CN radicals by laser-induced fluorescence (LIF) spectroscopy indicates that increases in CN radical production due to increases in the pressure of the precursor gas or applied rf power give way to plateau behavior at higher values for both pressure and power. LIF measurements of the rotational temperature of CN radicals yield values near 320 K, suggesting that the rotational energy of CN radicals is re-distributed to maintain near-equilibrium conditions in the plasma. These data, along with film formation and characterization studies, will be discussed with respect to the information that they provide about the deposition process and their implications for continuing work in this area.

## Plasma Science and Technology

## Room: 607 - Session PS2-TuM

## Advanced Gate Etch

**Moderator:** T. Kropewnicki, Freescale Semiconductor

8:00am **PS2-TuM1 Reaction Mechanisms in Patterning Hafnium Aluminate High-k Thin Films**, ***R.M. Martin****, University of California at Los Angeles, *H.-O. Blom,* Uppsala University, Sweden, *J.P. Chang*, University of California at Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium-based oxides, for sub-45nm CMOS devices. Hafnium aluminates ($Hf_{1-x}Al_xO_y$) have arisen as a promising material for gate oxide replacement due to their high dielectric constant, bandgap, and recrystallization temperature. Hafnium aluminates with the $Al_2O_3$ content varying from 0 to 100% were synthesized to study the effect of alumina addition to hafnia. An electron cyclotron resonance high density plasma reactor was used in this work to study the etching of hafnium aluminates in chlorine-based chemistries. The plasma density, electron temperature, and gas phase reactive species were characterized by a Langmuir probe, optical emission spectroscopy, and quadrupole mass spectrometry (QMS). $Hf_{1-x}Al_xO_y$ films were etched in $Cl_2$ and $BCl_3$ plasmas and the etch rate scaled linearly with the square root of ion energy at high ion energies (> 50 eV), however the etch rate in $BCl_3$ was 1.5 to 2 times that in $Cl_2$. The faster etch rate in $BCl_3$ was attributed to a change in the dominant ion from $Cl_2^+$ to $BCl_2^+$ as determined by QMS. At low ion energies, (< 50 eV), a physical-sputtering-like process was observed in $Cl_2$ while deposition was observed in $BCl_3$. The dominant metal-containing etch products were $HfCl_x$ and $AlCl_x$ in $Cl_2$ plasma and $HfCl_x$, $HfBOCl_4$, $AlCl_x$, and $Al_2Cl_x$ in $BCl_3$ plasmas, and increased with ion energy. Oxygen was detected removed in the form of ClO in $Cl_2$ and $(BOCl)_3$ in $BCl_3$ plasmas. The etching threshold energy can be tuned by about 2 eV by changing the film composition, making it possible to design a composiiton near the interface to maximize the etching selectivity with respect to silicon. Chlorine was measured on the surface of all etched films (0-3 at. %) as well as boron (~7 at. %) for the $BCl_3$-etched films. 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. Finally, a generalized phenomenological model will be presented to elucidate the effect of $Al_2O_3$ addition on modifying the etching characteristics of $HfO_2$.

8:20am **PS2-TuM2 Tungsten and Tungsten Nitride Etch Characterization for sub 45nm Metal Gate**, ***T. Morel***, STMicroelectronics France, *S. Barnola*, CEA-LETI France, *O. Joubert*, CNRS/LTM France

Continuing downscaling of structures involved in advanced CMOS devices brings new complexity in plasma etching processes. The introduction of new materials, (metal gates, high-k dielectrics) to avoid the poly depletion effect and to minimize the equivalent oxide thickness, requires new dry etch approaches. Innovation proposed here is the use of thin MOCVD tungsten or tungsten nitride layers (10nm) to achieve PMOS devices on 300mm wafers. In this work, we characterized both metal layers by angle resolved X-ray Photoelectron Spectroscopy (XPS) and X-Ray Reflectometry (XRR). It is found that W and WN layer present differences in terms of oxygen and carbon concentration and density. To get a better understanding of interfaces between the different layers of a complete gate stack (Poly-Si / TiN / WN or W / high-k), Secondary Ion Mass Spectroscopy (SIMS) and XPS depth profiling were performed. The characterization of as-deposited and integrated tungsten alloy revealed variations between both metals that involved two different strategies to achieve good profile in patterned metal gate electrode. Concerning the process development, etch rates of W and WN were carried out in chlorine and fluorine based chemistries on a 300mm ICP tool with in-situ optical emission spectroscopy and in-situ interferometer. With the support of ion mass spectroscopy and quasi in-situ XPS, etch mechanisms of tungsten alloy were identified. Finally, the integration of W and WN etch into a multiple steps process for sub 45nm metal gates were investigated. $Cl_2$-$O_2$ and $Cl_2$-$O_2$ with additional fluorine are the proposed solutions to control, respectively, the profile of tungsten nitride and tungsten, without damaging the passivation on the Poly-Si sidewalls.

8:40am **PS2-TuM3 Nitride Spacers Dry Etching for sub-20nm HfO2 - Metal Gate on Fully Depleted SOI**, ***C. Arvet***, STMicroelec., FR, *J. Chiaroni, V. Loup,* CEA-Léti/Minatec, FR, *P. Besson,* STMicroelec., FR, *P. Brianceau,* CEA-Léti/Minatec, FR, *M.P. Clement,* STMicroelec., FR, *V. Delaye, L. Tosti, C. Buj,* CEA-Léti/Minatec, FR, *O. Louveau,* STMicroelec., FR, *E. Vermande, M. Heitzmann, S. Barnola,* CEA-Léti/Minatec, FR, *R. Blanc*, STMicroelec., FR

Fully Depleted Silicon on Insulator is one of the most promising MOS transistors fabrication technologies to address low power and high speed applications challenges. Due to the very thin channel silicon thickness, selective epitaxial growth is mandatory to raise source and drain areas. So in addition to there classical uses as sidewall for ion implantation, spacers play a major role to avoid leakage current between metal gate and raised source and drain. On this way new constraints appear for nitride spacer dry etching. An accurate control of etch polymers is mandatory to allow a good performance of the next step, while a very high selectivity to thin silicon, silicon dioxide and HfO2 materials is required to avoid any silicon surface damage or HfO2 modification. Indeed, typical HfO2 thickness is less than 3 nm, thin silicon film is 10 nm or less while silicon dioxide hard mask on top of the gate must not be impacted. Moreover, two different approaches can be used for gate stack building. In the "spacer first approach", the nitride layer is deposited over the HfO2 material then spacers are etched, while in the "spacer last approach", the HfO2 is etched before nitride layer deposit. This affects the requirements for spacer etch, resulting in two different dry etch processes. These processes were developed in a DPS2 (Decoupled Plasma Source) Applied Material reactor either with a CH2F2 based chemistry or a CF4/HBr based chemistry. Etch rates, selectivities and non uniformities were optimized by adjusting gas ratio, source and bias RF power. SEM Cross sections, SEM-CD and TEM demonstrate good spacers profile and metal gate coverage. A 1.5 nm range spacer size control has also been reached, although spacer size adjustment by use of the overetch step seems to be limited. Plasma impact and selectivity to HfO2 and Silicon were measured by ellipsometry and XPS analysis. Results show no consumptions for HfO2 and less than 1.5 nm for silicon. A CFx polymer deposition allows high selectivities and no HfO2 modification. Post nitride dry etch XPS and particle measurement show also that HF wet chemistry is required to fully achieve High-K removal and optimize next integration steps. From these experiments, robust processes were developed. Electrical test of sub-20nm HfO2 and TiN Metal Gate on Fully Depleted SOI will be presented with the two integration schemes. This work has been carried out within the frame of Léti/Minatec-Crolles2 alliance program.

9:00am **PS2-TuM4 XPS Sidewall Analyses of Poly Si/TiN/$HfO_2$ Gate Stack Etched with Chlorine and Fluorocarbon Based Chemistries**, ***O. Luere***, Freescale Semiconductors, France, *L. Vallier, E. Pargon,* LTM-CNRS, France, *L. Thorsten*, Applied Materials

Patterning sub-40 nm metal gates on high k dielectrics is one of the biggest challenges for the fabrication of next generation devices. The metal gate etching step is, indeed, difficult: it must be highly anisotropic to maintain a tight CD control (≤ 2 nm) and must not damage the underlying high k material. In this work, we have investigated and compared the impact of the etching of the TiN layer in a Poly Si/TiN/$HfO_2$ gate stack using $Cl_2$/HBr and $SF_6/CH_2F_2$ based chemistries. The experimental work has been performed on a 200 mm etch platform connected, under vacuum, to an x-ray photoelectron spectroscopy surface analysis system. In order to better understand the etching mechanisms, we have used a technique based on X-ray photoelectron spectroscopy (XPS) to analyse the passivation layer deposited on the sidewalls of the patterns during the Polysilicon etching step and investigate its modification during the TiN etching step. We also used SEM pictures to analyse the gate profiles and determine the thickness of the passivation layer. The etching of polysilicon with a $Cl_2$/HBr based chemistry requires the introduction of $O_2$ in the plasma in order to form a SiOClBr layer which protects the polysilicon sidewalls. On the contrary, the etching of TiN must be $O_2$ free to prevent the metal oxidation. The absence of oxygen in the plasma gas phase during TiN etching can potentially lead to a modification of the passivation layer formed on the Polysilicon sidewalls. Nevertheless, We have shown that, using appropriate plasma conditions, the SiOClBr layer deposited on the chamber walls during Polysilicon etching is eroded during the TiN etch step, leading to an increase of the passivation layer thickness on the Polysilicon sidewalls. Same analyses using a $SF_6/CH_2F_2$ based chemistry will also be presented.

9:20am **PS2-TuM5 Reactive Ion Etching of Ru Compounds Modified by Ion Implant**, ***C. Park***, *B.S. Ju, S.C. Song, M. Cruz,* SEMATECH, *B.H. Lee, R. Jammy*, IBM

One of the technical hurdles for implementing high-k / metal gate in advanced CMOS is high threshold voltage ($V_{th}$) in p-MOSFETs. Recently, it was shown that the $V_{th}$ of p-MOSFETs can be lowered by using Ru compounds as a metal gate on HfSiO high-k dielectric. Gate etch requires good local and global etch uniformity across the wafer without damaging

***** PSTD Coburn-Winters Student Award Finalist

the underlying gate dielectric. Unlike Ru or $RuO_2$ films, Ru compounds have high etch resistance with conventional etch chemistries, which imposes a significant technical challenge on gate stack patterning. It is possible to etch Ru compounds by applying higher than normal bias power. A high bias power etch, however, poses the high risk of forming either a micro-trench or footing on the pattern sidewall and causing a rough patterned sidewall as well as punch-through of the gate dielectric. It was demonstrated that ion implant could modify the bond structure of Ru compounds, so that they could be etched in a highly controlled manner with $O_2/Cl_2$ plasma. Optimum implant condition, which enables plasma etch of the Ru compounds, was found by splitting of implant energy and dose conditions. The effects of the ion implant on film thickness, bonding of Ru compounds, and knock-on of Ru compounds and gate dielectric into silicon substrate were also studied.

9:40am **PS2-TuM6 Plasma Etching Processes for Aggressively Scaled Gate Features**, ***N.C.M. Fuller***, *M.A. Guillorn, Y. Zhang, W.S. Graham, E.M. Sikorski*, IBM TJ Watson Research Center

Scaling of device dimensions for 32nm and beyond technology nodes demands process, integration and tooling innovations to meet feature profile, line edge roughness (LER) and line width roughness (LWR) requirements. To these ends multi masking schemes have been employed to attempt to enable scaled devices and reduce LER/LWR constraints. Further, we have utilized various process conditions to increase the mechanical integrity of patterning materials in such multi masking schemes patterned with mixed electron beam and optical lithography. This methodology has enabled 20nm gates on a 60nm pitch with 0.5-1.0nm improvement in post lithography LER/LWR and 100% physical yield. These and other results will be presented and discussed.

10:40am **PS2-TuM9 Investigation of 45nm Silicon Gate Etching Process Variability Contributors**, ***L. Babaud***, Freescale Semiconductor, France, *P. Gouraud*, STMicroelectronics, *O. Joubert, E. Pargon*, CNRS/LTM, France

In a semiconductor world more and more aggressive in term of device performance and market cost, the control of critical dimension for 45 nm poly gate and beyond appears as a big challenge. Indeed as conventional photolithography is not able to define the novel design targets, other strategies as the double patterning on complex stack are developed. But the introduction of such complex process will induce additional sources of dimension variability and so alter the final functionality of the device. In this way, the research of the variability contributors from lot to lot, wafer to wafer, site to site will be the keys of an understood and controlled process. Some new parameters such as Line Edge Roughness (LER) will have to be considered. This presentation will focus on profile and dimension variability studies of the different steps of a gate stack process integrating a Hard Mask. Moreover we will investigate the impact of the 300 mm industrial ICP chamber walls conditioning strategies on the gate morphology. Chemical topography analyses by X-Ray Photoelectron Spectroscopy (XPS) will be performed to correlate the morphological results with passivation layer composition, deposited during the silicon etch process.

11:00am **PS2-TuM10 Control of $SiO_2$/Si Interface States during Plasma Etching Processes**, ***Y. Ishikawa***, *Y. Ichihashi*, Tohoku University, Japan, *S. Yamasaki*, National Institute of Advanced Industrial Science and Technology, Japan, *S. Samukawa*, Tohoku University, Japan

Plasma processes are indispensable in the fabrication of MOS LSI devices. During plasma processes, however, serious problems can occur, such as charge-build up damage and UV photon irradiation damage. In particular, UV irradiation from the plasma causes drastic degradation of sub-50nm MOS LSI device characteristics, because the penetration depth of UV photons into dielectric films is more than 10nm. We have previously reported that UV photons from plasma effectively generate E' centers (Si dangling bond in SiO2 film) in SiO2 films. However, the relationship between UV irradiation from plasma and interface states' (Pb centers, Si dangling bond at SiO2/Si interface) densities must be basically understood during the plasma process, because the generation of interface states directly degrades the electronic properties of MOS LSI devices. We focus on SiO2/Si interface state density trends during conventional continuous wave (CW) plasma and pulse-time-modulated (TM) plasma etching processes. In order to evaluate the generation of interface state density, 5nm thick thermally grown SiO2 films were formed on Si substrates. The SiO2 films were then irradiated using Ar inductively coupled plasma. After that, we evaluated the Pb centers using electron spin resonance spectroscopy. Before the plasma irradiation, the density of the Pb centers was less than $1x10^{10}$ $cm^{-2}$ spins. After the Ar CW plasma irradiation, and without any substrate RF bias power, Pb centers drastically increased. That is, the Pb centers increased drastically even after irradiation using conventional Ar CW plasma and elimination of ion bombardment. We also investigated the dependence of ion bombardment energy on the density of Pb centers in conventional CW plasma. However, even when 100W of RF power was applied during the plasma process, the ESR spectrum did not change. This result indicates that Pb centers are mainly generated by irradiation with UV photons during plasma processes. Therefore, we investigated the effects of TM plasma on eliminating Pb centers. During the TM plasma irradiation, the UV photon irradiation was drastically reduced during the plasma's "off" period. After the TM plasma irradiation, the Pb centers densities reduced dramatically to less than $1x10^{10}$ $cm^{-2}$ spins, compared to those observed after CW plasma irradiation. We found that TM plasma was the most promising candidate for the elimination of Pb centers during the plasma etching processes.

11:20am **PS2-TuM11 Plasma Etching in the Era of Intensive Integration Innovation**, ***Th. Lill***, Applied Materials, Inc. **INVITED**

Driven by relentless pursuit of Moor's law, plasma etching advances at a rate never before seen in the history of this IC processing technology. New challenges are posed by several significant co-emerging trends: 1. Pattern fidelity requirements within wafer and lot reach sub nanometer, i.e. atomic resolution. 2. Plasma Etching is now an integral part of pattern generation (resist trim, double pattering, multilayer resist schemes). 3. Aspect ratios increase almost inverse proportional to the nominal line width for any given technology node reaching 100:1 for capacitor silicon etches and 40:1 for capacitor dielectric etches. 4. The number of potential new material candidates and their possible combinations in future stacks is exploding. At a first glance these challenges are well known and represent just another incremental tightening of known requirements. In this paper, we will show that these trends lead to three new paradigms in plasma etching: divergence of plasma etch applications, convergence the required process space to cover these applications and the need for precision chamber matching. We will discuss the consequences for plasma etch engineers and show examples for how Applied Materials Etch is responding to these new paradigms today to provide productive solutions for whatever device and integration engineers hold in store for the plasma etch community.

12:00pm **PS2-TuM13 The Effect of Oxygen Addition in a Chlorine Plasma during Shallow Trench Isolation Etch**, ***C.C. Hsu***, *J.P. Chang*, University of California at Los Angeles

Shallow trench isolation has been widely used to electrically isolate adjacent transistors. The mixtures of chlorine and oxygen have been one of the most commonly used chemistries for the shallow trench isolation etching process. In this work, an electron cyclotron resonance high density plasma is used to study the effect of oxygen addition in a chlorine plasma during the etching of silicon. To quantitatively assess the effect of oxygen addition, the plasma density and the electron temperature were characterized by using a Langmuir probe. The plasma species, including the etching by-products, were studied using the quadrupole mass spectrometry and the optical emission spectroscopy. The silicon etching rate was measured in-situ by using laser interferometry. Scanning electron microscopy was used to observe the topography change of the etched blanket films. The silicon etching rates were found to increase with the square root of the ion energy with a 9 eV threshold energy, suggesting the etching reaction is limited by the momentum transfer from the ions to the surface. With a relatively small amount of oxygen addition to the chlorine plasma, the etching rate remained approximately constant while the by-product identity and its distribution changed significantly. The dominant ionic etching by-products in chlorine plasmas were $SiCl^+$ and $SiCl_3^+$, but changed to $SiCl^+$, $SiOCl_2^+$, and $SiCl_3^+$ with the oxygen addition. The roughness of the etched surface increased significantly with oxygen addition. The significant changes of the by-products distribution and the etched surface topography suggest that the etching mechanism changes with the oxygen addition to the chlorine plasmas.

# Tuesday Afternoon, October 16, 2007

**Plasma Science and Technology**

**Room: 606 - Session PS1-TuA**

**Plasma Etching for Advanced Interconnects II**

**Moderator:** D.J. Economou, University of Houston

1:40pm **PS1-TuA1 Process Performance of $CO_2$ In Situ Photoresist Ashing Processes and Their Influence on ULK Materials Modifications**, ***M.S. Kuo***, *G.S. Oehrlein*, University of Maryland at College Park, *S. Sirard, E.A. Hudson*, Lam Research Corp.

An in situ ashing process for removing photoresist (PR) layers is desired by industry as an alternative to remote plasma ashing processes since it could be more easily integrated with plasma etching processes. In this work, we examined the feasibility of $CO_2$ as source gas for in situ PR ashing processes compatible with ULK materials, and performed characterization of 193 nm PR ashing along with ULK (JSR LKD 5109, and several other candidate materials) damage evaluation. Reducing $CO_2$ pressure from 100 to 10 mTorr increased the ion density and led to a higher PR ashing rate (substrate at 10 °C, line of sight interaction), while suppressing ULK damage (non-line-of-sight interaction). Low pressure operation using $CO_2$ enabled a high ashing efficiency (AE) which is defined as the amount of PR removed over the amount of ULK material damaged (for a given time). The $CO_2$ AE at 10 mTorr is ~5 times improved relative to $O_2$ and comparable to the best values we have measured for typical $H_2$ based remote plasma ashing processes. For the $CO_2$ in situ ashing processes, we examined sidewall damage introduced in ULK trench structures employing scanning electron microscopy (SEM). We also used a gap structure to simulate exposure of ULK materials in actual trench sidewalls. This allowed characterization of ULK surface modifications induced by the indirect plasma exposure using ellipsometry, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). These results will be presented, along with a discussion of issues derived from real pattern transfer processes such as etching/ashing interaction and the influence of slight ion bombardment to ULK sidewall during in situ ashing.

2:00pm **PS1-TuA2 SiOCH Damage in $N_2/H_2$ Plasma**, ***M. Fukasawa***, *T. Tatsumi, K. Nagahata*, Sony Corporation, Japan, *S. Uchida, S. Takashima, M. Hori*, Nagoya University, Japan, *Y. Kamide*, Sony Corporation, Japan

Reducing the damage to low-k dielectrics caused by plasma is one of the key issues for achieving high-performance devices. We report the root cause of the dielectric constant increase (Δk) of SiOCH that occurs after $N_2/H_2$ plasma exposure. The plasma damage of SiOCH (k=2.65) was investigated in a dual-frequency (60/2 MHz) capacitively coupled plasma reactor equipped with a surface wave probe, quadruple mass spectrometer, high-voltage probe and optical emission spectroscope. Measurements were performed as a function of an $N_2/H_2$ flow rate ratio, while maintaining total ion and neutral fluxes, and ion energies. The amount of moisture uptake during air exposure, Δk, water contact angle, and chemical bonding were analyzed. The behavior of Δk strongly depends on the $N_2/H_2$ flow rate ratio. Thermal disorption spectroscopy revealed that the Δk is almost proportional to the amount of moisture uptake.[1] The amount of Si-$CH_3$ bond in the bulk SiOCH measured by FT-IR decreased monotonically with an increasing $H_2$ flow rate ratio. These results suggest that the Si-$CH_3$ bonds were broken by H, and the dangling bond (or one weakly terminated by H) was generated during plasma exposure. During air exposure, the Si-H bonds are replaced with Si-OH bonds, which then adsorb moisture. However, in the case of H-rich plasma, the Δk decreased, while the total number of adsorption sites increased. We analyzed the depth profile of incident ions since the SiOCH damage gradually varies from the surface depending on the depth distribution of ion, light, and radical diffusion from the surface. In relatively H-rich plasma, the small mass number of dominant ion species ($H_3^+$) results in the deeper damage caused by the longer projected range (10 nm). Thus, more Si-$CH_3$ bonds remained on the surface and generated more hydrophobic surface, compared with that generated by relatively N-rich plasma. The hydrophobic surface was found to suppress the moisture permeability and lead to the Δk reduction. To suppress Δk, it is important to precisely control the incident radical/ion flux ratios and ion energies thus reducing the adsorption sites in the bulk and keeping the hydrophobic surface that suppresses the water permeation during air exposure.

[1]M. Fukasawa et al., in Proceedings of International Conference on Dry Process, Nagoya, Japan (2006) p.5.

2:20pm **PS1-TuA3 Study of Downstream $O_2$ Plasma Damage to Blanket and Patterned CDO Low k Films**, ***J. Bao***, *H. Shi, H. Huang, J. Liu, P.S. Ho, E. Paek, G.S. Hwang*, The University of Texas at Austin

Carbon Doped Oxide (CDO) low k films were treated by downstream $O_2$ plasma. The effects of $O_2$ plasma on blanket and patterned low k dielectric surfaces were studied by in-situ angle resolved X-ray photoelectron spectroscopy (ARXPS) and Fourier transform infrared spectroscopy (FTIR). The reaction byproducts were analyzed by residual gas analyzer. Roles of ions and radicals in the plasma to cause carbon depletion were investigated using a plasma source that was capable of separating ions from plasma beam. Energetic ions in oxygen plasma contributed much to the loss of film hydrophobicity and dielectric constant through the formation of C=O and Si-OH. Coupled with RGA analysis, three possible reaction paths leading to carbon depletion were proposed. Effects of ions and radicals on blanket low k films at different tilt angles ($0^0$ to $90^0$) were analyzed. Finally, $O_2$ plasma damage to patterned CDO film was studied by XPS and SEM. And the damage behavior was simulated with Monte Carlo method. It was found that the charging potential distribution induced by plasma was important in determining low k film carbon loss. The charging potential distribution was mainly related to the geometry of low k trench structures.

2:40pm **PS1-TuA4 Ion- and Radical-Induced Ultra Low-k Damage Mechanisms**, ***M.A. Goldman***, *S.H. Kim, D.B. Graves*, University of California, Berkeley

It is widely understood that photoresist strip following dielectric etch often damages ultra low-k films. We measured the effects of molecular beams of ions and radicals impacting porous, ultra low-k dielectric films in a vacuum beam chamber to simulate damage induced by photoresist stripping under controlled conditions. Damage was characterized by ex-situ FTIR, contact angle measurements, SEM coupled with damaged layer etching, and AFM. We find that rare gas ions ($Ar^+$ and $Xe^+$) alone appear to damage only the near-surface region of the film. In addition, we report results on the mechanism of damage due to radical beams, including O, N, $NH_x$, NO, and H. For oxygen radical damage on porous ultra low-k films, carbon abstraction and subsequent moisture uptake is shown to be a diffusion-limited process that occurs as a front of carbon depletion that penetrates through the film. Rare gas ion bombardment at normal incidence is shown to significantly reduce the damaging effects of O atoms, apparently by closing pores at the surface of the film.

3:00pm **PS1-TuA5 Evaluation of Plasma Damages due to VUV Light, UV Light, Radicals, Ions and Interaction of Light and Radicals on Low-k Films**, ***S. Uchida***, *S. Takashima, M. Hori*, Nagoya University, Japan, *M. Fukasawa, K. Oshima, K. Nagahata, T. Tatsumi*, Sony Corporation, Japan

The low-k films are wildy used as the insulating materials of ULSIs in order to reduce the RC delay. 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 order to realize the damage free plasma processes, it is necessary to clarify the influences of the light, the radicals, and the ions from the plasmas on the low-k films. In our previous study, in order to separate the effects of the light, the radicals, and the ions in the process plasmas, we have developed a new technique, where the four kinds of etching samples were prepared. We call the technique a pallet for plasma evaluation (Pape). These samples were as follows. The $MgF_2$ and the quartz windows were put directly on the film, respectively, to clarify the influence of the vacuum ultraviolet (VUV) light and the ultraviolet (UV) light from the plasmas. The $MgF_2$ and the 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 the light, the radicals, and the ions, nothing was put on the film. In this study, we have improved the Pape in order to evaluate the effect of the interaction of the light and the radicals. The advanced Pape is the methods of putting the $MgF_2$ and the quartz windows 0.7 mm above the film surface. The low-k film used in this study was the porous SiOCH film. The dual frequency capacitively coupled plasma employing $H_2$ and $N_2$ gases was used in this study. 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 of 50%, and a pressure of 5.3 Pa, the ions induced the largest damage on the films. Moreover, the damage due to the interaction of the lights and radicals was larger than that due to the individual lights and radicals.

4:00pm **PS1-TuA8 Low-Damage Low-k Etching by $CF_3I$ Plasma with Low Global Warming Potential**, ***E. Soda***, *S. Kondo*, Selete, Japan, *Y. Ichihashi*, *A. Sato*, *H. Ohtake*, *S. Samukawa*, Tohoku University, Japan, *S. Saito*, Selete, Japan

The $CF_3I$ gas has been developed to reduce the recent global warming[1] because it has a low global warming potential (GWP) of 1.0 while most of conventional etching gases have considerably higher potentials of more than 1000 ($CF_4$: 6500, $C_4F_8$: 8700). The feasibility of $CF_3I$ plasma etching and its damage to the porous low-k film (SiOC, k=2.6) were studied in this work. When an SiOC film was exposed to the $CF_3I$ plasma, increase in the k-value and decrease in $CH_3$ group of the film (FTIR) were found to be suppressed compared with those caused by conventional $CF_4$ plasma because intensity of the ultra violet (UV) light in $CF_3I$ plasma was lower than that of $CF_4$ plasma. To investigate etching property of $CF_3I$ gas, we used a photolithography patterned wafer with the resist mask of 200-nm pitch size. As a result, the etching profile of $CF_3I$ plasma was comparable with that of $CF_4$ plasma. Since the etching selectivity (SiOC/ArF) of $CF_3I$ plasma was higher than that of $CF_4$ plasma, the remaining resist thickness after etching increased, thereby line edge roughness (LER) was suppressed. Moreover, the pulse operation in $CF_3I$ plasma drastically increased etching rate and minimized UV damage to the low-k film because injection of negative ions in pulsed plasma enhanced the low-k film etching. Accordingly, we found that $CF_3I$ plasma is one of the promising candidates for low-damage and highly selective low-k etching. This work is supported by the New Energy and Industrial Technology Development Organization (NEDO).

[1]N. Nagasaki et al., "The Development of a Novel Catalytic Technology for $CF_3I$ Manufacture", Halon Options Technical Working Conference, May 2000.

4:20pm **PS1-TuA9 Ash Plasma Exposure of Hybrid Material (SiOCH and Porogen): Comparison with Porous SiOCH**, ***M. Darnon***, CNRS, France, *T. Chevolleau*, LTM-CNRS, France, *T. David*, CEA-LETI-MINATEC, France, *L. Vallier*, LTM-CNRS, France, *J. Torres*, STM, France, *O. Joubert*, LTM-CNRS, 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 etch and ash plasma exposure and one of the major integration challenges is to reduce the impact of plasma processes on the ultra low-k degradation. To solve this issue, one of the emerging solutions is the late porogen removal process. In this approach, the porosity is generated by a sacrificial carbon based porogen which is desorbed after patterning or copper filling. Such hybrid materials (SiOCH matrix and porogen) are expected to behave like dense materials and therefore to be less sensitive to plasma processes (etching and ashing). In this work, the hybrid material and the porous material are compared in terms of sensitivity to ash plasmas. The ash plasmas are performed in an industrial MERIE (Magnetically Enhanced Reactive Ion Etcher) and in an ICP (Inductively Coupled Plasma) reactor using oxygen-, ammoniac- or methane-based plasmas. X-ray photoelectron spectroscopy studies shows that the surface composition of the porous SiOCH is modified after the ash plasma treatments (SiO, SiON, and SiOC after $O_2$, $NH_3$ and $CH_4$ treatments, respectively) and X-ray reflectometry measurements indicate an increase of the surface density. Hybrid materials and porous SiOCH after ash plasma treatments present similar surface composition but no surface densification is evidenced. After the pore release process of the treated hybrid material, the surface composition remains close to the treated porous SiOCH and the top surface is denser than as deposited porous SiOCH. Infrared spectroscopy (FTIR) shows an important bulk modification of the porous SiOCH after ash plasma exposure (carbon depletion and new absorption bonds depending on ashing plasmas), whereas the hybrid material volume is hardly modified. After the pore release process of the treated hybrid materials, FTIR spectra are identical to an untreated porous SiOCH indicating an almost unmodified porous SiOCH. The porogen of the hybrid material prevents the bulk modification potentially induced by the different ash plasmas. Consequently, after the pore release process the material is similar to an unmodified porous SiOCH with only a slight modification of the top surface.

4:40pm **PS1-TuA10 Effects of Combining H Radical Treatment and Low-k Restoration for Extreme Ultra Low-k**, ***L.H. Chen***, *S. Tahara*, Tokyo Electron AT LTD, Japan, *R. Asako*, Tokyo Electron LTD, Japan, *K. Yamazaki*, Tokyo Electron AT LTD, Japan, *Y. Ohsawa*, Tokyo Electron LTD, Japan, *Y. Chiba*, Tokyo Electron AT LTD, Japan, *H. Nagai*, Tokyo Electron LTD, Japan, *K. Kubota*, Tokyo Electron AT LTD, Japan, *K. Maekawa*, Tokyo Electron LTD, Japan

Extreme Ultra low-k (eULK) dielectrics with k-value of below 2.2 have been extensively evaluated for 32 nm technology and beyond. The eULK dielectrics exert new challenges in etch/ash plasma process and post treatment process. In photo resist stripping, hydrogen radical is known as a reactant to minimize low-k damage compared to oxygen. Hydrogen radical, however, does not restore etch-induced low-k damage. Thus, a low-k restoration following to hydrogen radical stripping should be processed subsequently. At this point, we picked up the silylation process with vaporized silazanes as a low-k restoration technique so that all processed from etch to low-k restoration could be integrated in a dry system for high restoration effectiveness and productivity. In this study, we investigated the effects of combining H radical treatment and low-k restoration by using spin on dielectric blanket film (k=2.2). It was confirmed that a hydrogen process/treatment did not only minimize low-k damage in photo resist stripping but also reduce oxygen in copper, and decrease fluorine in low-k film by Thermal Desorption Spectroscopy (TDS) analysis. Moreover, the combination of a hydrogen treatment and low-k restoration in a dry system without air exposure showed that k value, leakage current, H2O degas amount by TDS, and carbon profile by Secondary Ion Mass Spectroscopy (SIMS) were improved and recovered to near pristine low-k material.

5:00pm **PS1-TuA11 Process Induced Damages and Their Recovery for Highly-Porous Self-Assembled Porous Silica Low-k Film**, ***K. Kinoshita***, *S. Chikaki*, *M. Nihei*, Selete Inc., Japan, *H. Tanaka*, *K. Kohmura*, Mitsui Chemicals, Inc., Japan, *T. Nakayama*, ULVAC, Inc., Japan, *T. Kikkawa*, ASRC, AIST, Japan

To realize the low-k film of k<2.1 with silica material, it is necessary to achieve the porosity higher than 50%. We have been developing porous silica materials. The characteristics of the porous silica is; (a) scalability of the k-value by controlling pore structure with self-assembled process, and (b) post reinforcing and hydrophobizing treatment.[1] The new process technologies to apply such highly porous low-k films to the interconnect module process have been developed, simultaneously. Especially, introduction of the damage recovery process is inevitable.[2] This paper describes about damage recovery process for the porous silica materials. The porous silica blanket films with k~2.07 and E~6.5 GPa were formed on 300 mm wafers. They were half-etched by fluorocarbon plasma, and were exposed to high-temperature $He/H_2$ down flow ashing plasma. Then, wet clean by two different types of chemical were examined, followed by the damage recovery process by TMCTS vapor annealing. The samples were evaluated by k-value measurement, FT-IR, and TDS after each step. The porous silica films after the etching and the ashing were first treated by the organic acid type wet chemical solution. The k-value of the films increased from 2.07 (pristine) to 2.66 (etching), 2.67 (ashing), and 2.96 (wet clean). The TDS spectrum showed the desorption of the species originated in the wet chemical solution. In contrast to that, the k-value increased to 2.78 after the treatment by the dilute aqueous solution type chemical. The FT-IR and TDS spectra showed almost no change compared with those after the ashing. The recovery process at the pressure of 4 kPa or 30 kPa were evaluated. The recovery of the k-value was remarkable under the high pressure 30 kPa conditions (k=2.17). The collision probability enhancement between silanol groups on the pore surface and TMCTS molecules diffusing into the pore is important to improve recovery effect. When the incident ion-energy during etching was reduced to change the initial damage level with keeping final film thickness, the k-value recovered clearly at the lower ion-energy condition. The recovery effects by the other molecules, and electrical properties of Cu interconnect structure will be presented. Part of this work was assisted by NEDO.

[1]K. Kohmura, et al., Thin Solid Films, 515, 5019 (2007)
[2]T. Ono, et al., Jpn. J. Appl. Phys., 45, 6231 (2006).

## Plasma Science and Technology

## Room: 607 - Session PS2-TuA

## Plasma Sources

**Moderator:** D.L. Keil, Lam Research Corporation

1:40pm **PS2-TuA1 Influence of Gas Heating on Microplasma I-V Characteristics**, ***S.G. Belostotskiy***, *V.M. Donnelly*, *D.J. Economou*, University of Houston

Experimental I-V characteristics of DC microdischarges in helium were obtained at different operating pressures (P = 300 - 800 Torr). Since the interelectrode gap was relatively small (L = 300 μm), the voltage drop across the discharge was approximately equal to that across the cathode sheath. It was found that the scaling laws obtained by the classical theory of the cathode layer developed by von Engel and Steenbeck (i.e., the cathode voltage is a function of current density divided by the square of the pressure - $V_c = f(j/p^2)$) are not applicable to microdisharges due to the influence of gas heating. For example, the voltage drop at p = 700 Torr was 40 Volts higher than that at p = 300 Torr for the same reduced current density J = 3

$\mu A/(cm^2*Torr^2)$. A new semi-analytical model of the cathode layer that accounts for neutral gas heating was developed. Model predictions were in agreement with the experimental I-V characteristics. The model can be used to quantify the influence of neutral gas heating on microdischarge performance.

2:00pm **PS2-TuA2 RF Discharge under the Influence of a Magnetic Field**, ***E.V. Barnat***, *P.A. Miller*, Sandia National Laboratories, *A.M. Paterson*, Applied Materials

We examined the effects of an externally applied magnetic field (0 to 150 Gauss) on a capacitive 13.56 MHz argon discharge in a Gaseous Electronics Conference (GEC) reference cell. The electrical characteristics of the discharge were measured as functions of applied magnetic field and rf power. At fixed power the rf voltage decreased with increasing magnetic field. The discharge impedance was predominantly capacitive and became more resistive as the electron mobility decreased with increasing magnetic field. We also measured the effect that the magnetic field had on the spatial distribution of the plasma in vertical planes parallel and perpendicular to the direction of the magnetic field using Langmuir probes, optical emission, and laser induced fluorescence. Due to ExB forces, the distribution of excited states in the plasma remained radially symmetric in the plane parallel to the magnetic field and became skewed in the plane perpendicular to the magnetic field. The degree of skew depended on the state probed. Finally, we examined the temporal evolution of the electric fields in the plasma. In the presence of magnetic field, the sheath thickness decreased and most of the voltage drop was contained within the sheath. Consistent with dc voltage trends, there was no significant sheath reversal observed at higher magnetic fields. Comparisons of the results presented here are made to trends predicted by models and simulations found in the literature.

2:20pm **PS2-TuA3 Characterization of a High Power Surface Wave $O_2/N_2$ Plasma Jet for Removing Photoresist from Semiconductor Wafers**, ***M. Bhargava***, *B. Craver*, *H. Guo*, University of Houston, *A.K. Srivastava*, Axcelis Technologies, *J.C. Wolfe*, University of Houston

We describe a plasma system for removing photoresist from silicon wafers where reactant gas flowing in a quartz tube is activated by a high power, 2.45 GHz surface wave discharge at pressures near 80 Torr.The plasma applicator is based on Moisan's 'surfaguide' design[1] where the discharge tube passes through a thin-walled coupling aperture in a reduced-height wave-guide section. Microwave electric fields loop out of the aperture and launch surface waves in both directions along the interface between the discharge tube and the plasma. The directional flow (3slm) of process gas in the tube (6 mm inside diameter) effectively suppresses the discharge on the upstream side of the waveguide. This same flow, in conjunction with the downstream surface wave, produces a plasma jet that emerges from the end of the discharge tube and carries hot, activated gases to a scanning wafer below.The discharge tube is cooled by a counter-flow of clean, dry air confined in a coaxial outer tube; this enables extended operation at 2.5 kW for $O_2/N_2$ discharges. The wafer is clamped to a heated, 200 mm chuck with a backside pressure of about 35 Torr. An x-y stage, actuated by in-vacuum linear motors, translates the wafer with speed and acceleration up to 1.1 m/s and 2 g, respectively. The efficiency of converting microwave power to thermal jet power is 21% and 19% for respective substrate-to-source distances of 0.9 cm and 2.9 cm, independent of oxygen concentration. For an $O_2$:$N_2$= 9:1 plasma jet operating at 2.5 kW, 80 Torr pressure, and a flow of 3slm, the etched track profile is Gaussian in shape with a full-width-at-half-maximum of 1.5 cm. A serpentine raster pattern with 7 mm pitch is used to cover an entire 200 mm wafer. The time to clear 1.2 µm thick, unimplanted photoresist is about 10 seconds for a 70 cm/s scan speed and 200 °C chuck temperature. This corresponds to an instantaneous etch rate of about 4000 µm/min. A detailed analysis of the transient heating process will be presented at the conference. Acknowledgements: Partially supported by the Texas Center for Superconductivity at the University of Houston. The authors are grateful to Ivan Berry for insightful discussions. The opinions expressed are solely the responsibility of the authors.

[1] M. Moisan et al., IEEE Trans. Plasma Sci. PS-12, 203-214 (1984).

2:40pm **PS2-TuA4 Effect of DC Superposition on the Selective Etching of $SiO_2$ over $Si_3N_4$ in Dual Frequency Capacitively Coupled Plasma**, ***S.-O. Lee***, *M.-S. Lee*, *S.-H. Cho*, *Y.-S. Cho*, *S.-C. Moon*, *J.-W. Kim*, HYNIX Semiconductor Inc., Republic of Korea

The characteristics of negative external DC superposition with the top electrode in dual frequency $C_4F_6/O_2/Ar$ gas capacitively coupled plasma (CCP) on the selective etching of $SiO_2$ over $Si_3N_4$ have been studied as a function of supplying DC voltage, ranging from 0V to -1500V. It is reported that the accelerated 2nd electron which is generated near top electrode sheath by using DC superposition irradiates the wafer, and polymer molecular structure such as C/F ratio and C-C bond structure etc. is reformed. To analyze the effect of DC superposition in dual frequency CCP source, we investigated the chemical species such as $CF_2$ radicals and other radicals that have influence on polymerization, in the gas phase with optical emission spectroscopy (OES). The thickness and components of fluorocarbon polymer on etched surface were investigated with high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS).

3:00pm **PS2-TuA5 Frequency and Pressure Effects in Plasma Etching of High Aspect Ratio Features in Dielectric Films**, ***E.A. Hudson***, *C. Hayden*, *D.L. Keil*, *S. Engelmann*, *C. Rusu*, *L. Romm*, *M. Srinivasan*, Lam Research Corp.

Microelectronics processing requires etching of many different dielectric films and structures. Among these applications, some of the most challenging are the etching of high aspect ratio contacts and memory cells. Dual-frequency capacitively-coupled discharges at high power are widely used for these applications. Typically a lower excitation frequency provides the capability for high energy ion bombardment while a higher frequency allows decoupled control of plasma density. This paper examines the effect of applying three different excitation frequencies at the wafer electrode to access this process regime, using a mechanically confined plasma in a narrow-gap etch reactor. The effects of process pressure and 27MHz vs 60MHz, in combination with 2MHz, were characterized by plasma diagnostic measurements of ion flux and radical densities. Dense arrays of high aspect ratio holes were etched to measure the feature-level influence of these process control parameters. Results indicate that the combination of 60MHz and lower pressure allows operation at higher ion:radical flux ratios, which may help to prevent early etch stop. Additionally the radical chemistry is controlled by the ratio of 27MHz to 60MHZ power. Therefore the combined use of three frequencies improves the tuning of feature profiles and the control of striations.

4:00pm **PS2-TuA8 Numerical Investigation of Wave Effects in High-Frequency Capacitively Coupled Plasmas***, ***Y. Yang***, *M.J. Kushner*, Iowa State University

The trend in dielectric etching using capacitively coupled plasmas is use of multiple frequencies where a high frequency (tens to hundreds of MHz) dominates ionization and a low frequency (a few to 10s MHz) is used to control ion energy distributions. As the effective wavelength in the plasma waveguide represented by the reactor decreases with increasing frequency, electromagnetic wave propagation effects become a concern and may give rise to limitations on processing uniformity. These effects have been investigated experimentally but are difficult to address computationally in arbitrary geometries due to the coupling between the electromagnetic and the electrostatic fields, the latter of which is responsible for the formation of the sheath. In this talk, we discuss results from a computational investigation of high frequency effects in capacitively coupled plasmas. A full Maxwell solver based on the concept of vector and scalar potentials, and capable of resolving wave effects in a self-consistent manner in arbitrary geometries, was developed and incorporated into the Hybrid Plasma Equipment Model, a two-dimensional hybrid simulation. In particular, the capability to address multiple frequencies in the time domain are included. To properly capture high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. The method of solution will be discussed and comparisons made to using a conventional electrostatic method for electric fields. Results from investigations of dual frequency CCPs (low frequency < 10 MHz, high frequency > 50 MHz) in 10s of mTorr polymerizing and non-polymerizing gas mixtures will be discussed. Assessments of the change in power deposition profile as a function of frequency will be made.

*Work supported by the Semiconductor Research Corp. and the National Science Foundation.

4:20pm **PS2-TuA9 Physics of Very High Frequency (VHF) Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *K. Bera*, *K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma (CCP) discharges are widely used for dielectric etching in the semiconductor industry. Operating frequencies, especially the source frequency in multi-frequency CCP systems, have generally increased in recent years to be able to generate high electron-density discharges with moderate ion energy. Concomitantly, economic considerations are driving towards radially larger plasma discharges. The combination of higher driving frequencies and larger plasma size means that electromagnetic effects start to play a more important role in determining plasma behavior. Understanding the physics of VHF plasmas is therefore critical for assessing the scalability of CCPs to future generations of dielectric etching technologies. This paper uses a computational model to elucidate the physics of VHF CCP discharges. The 2-dimensional model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential, A, are solved in the frequency domain after every cycle for multiple harmonics of the driving frequency.

Current sources for the vector potential equations are computed using the plasma characteristics from the previous cycle. The coupled set of equations governing the scalar potential, φ, and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron temperature equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. Our simulations focus on a 180 MHz CCP discharge, and examine the effect of inter-electrode spacing, driven electrode diameter, grounded electrode size and magnetic field on the plasma characteristics. It is found that the electrostatic component of the electric field peaks in the sheath region, where there is an imbalance between positive ion and electron concentrations. Electromagnetic fields are generated by current flowing through the discharge. The electromagnetic component of the electric field peaks in the center of the chamber due to the standing wave effect. The electromagnetic fields have a strong influence on charged species location and concentration at 180 MHz. However, besides the operating frequency, the plasma reactor design (inter-electrode spacing and electrode sizes) also determines the relative importance of the electromagnetic fields in plasma dynamics.

4:40pm **PS2-TuA10 Electron Heating Mechanisms, Mode Transitions, and Non-Uniformities in Dual Frequency Capacitive Discharges**, ***P. Chabert***, École Polytechnique, France **INVITED**

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. In some circumstances, a third frequency is added to further control the etching processes by modifying the ion energy distribution function at the substrate. In this paper, we focus on the consequences of multiple-frequency excitation on the electron heating mechanisms, and in turns on the plasma uniformity. We will discuss the collisionless and collisional electron heating mechanisms within rf sheaths, when they are driven by two frequencies. For typical discharge parameters, we find the result that the collisionless heating produced by the combination of two frequencies can be much larger than that of either acting alone. We will also address the issue of electromagnetic effects arising when the wavelength associated with the highest frequency becomes comparable to (or shorter than) the electrode size. In this situation, the electric field has two components, (i) the usual capacitive field perpendicular to the electrodes, (ii) and the inductive field, parallel to the electrode. The power deposited by the inductive field may be greater than the capacitive power. As in classical inductive discharges, the high frequency capacitive discharge experiences capacitive-to-inductive (E to H) transitions when the injected power, i.e. the voltage between the electrodes, is increased. Finally, both the capacitive and inductive powers are radially non-uniform, which can lead to severe problems of process uniformity.

## Plasma Science and Technology

## Room: 4C - Session PS-TuP

## Plasma Science and Technology Poster Session

**PS-TuP1 Selective Etching of $SiO_2$ over $Si_3N_4$ in Triple Frequency Capacitively Coupled Plasma System**, ***H.-G. Lee***, *S.-O. Lee, M.-S. Lee, S.-H. Cho, S.-K. Lee, S.-C. Moon, J.-W. Kim*, HYNIX Semiconductor Inc., Republic of Korea

It has been reported that the triple frequency (60MHz, 27MHz, 2MHz) capacitively coupled plasma (CCP) system provides more advanced process performance and wider process window for etching dielectric films compared to conventional dual frequncy (60MHz, 2MHz) CCP system. In this study, the effect of triple frequency with the bottom electrode in $C_4F_6/O_2/Ar$ gas plasma on the selective etching of $SiO_2$ over $Si_3N_4$ is considered as a function of the power applied to each frequencies. To understand the characteristics of triple frequncy concerning etch selectivity of $SiO_2$ over $Si_3N_4$, we considered the chemical species such as $CF_2$ radicals and other radicals that have influence on polymerization using optical emission spectroscopy (OES). The thickness of deposited polymers and components in this triple frequency CCP system were investigated by high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS).

**PS-TuP2 Etching Characteristics of $V_2O_5$ Thin Films using by $Cl_2$/Ar Inductively Coupled Plasma**, ***C.M. Kang***, *C.I. Kim*, Chungang University, Korea

Recently, the technology of microelectronic systems has attracted global attention for applications such as medical devices, communication systems, sensors and actuators. Vanadium oxide has a high capacity for ion storage, it is stable under a cyclic voltage and provides a particular (mixed) type of coloration complementary to that exhibited by the tungsten oxide ($WO_3$), allowing the production of high performances smart windows. Also vanadium oxides, with unique characteristic structures, comprise a particularly interesting group of inorganic 3d-transition metal oxide compounds due to their diverse, electronic, opto-electronic, electrochromic, and magnetic properties, which makes them potential candidates for important technological applications. Research and development of $V_2O_5$ have been rapidly accelerated to improve materials for the last decades. But, etch properties of $V_2O_5$ have not established yet. In this study, we investigated etch characteristics of dry etching of the $V_2O_5$ thin films in the inductively coupled plasma etch system with ($Cl_2$/Ar) gas mixture. The etching characteristics of $V_2O_5$ thin films were investigated in terms of etch rates and selectivity as a function of ($Cl_2$/Ar) gas mixing ratio, rf power, dc bias voltage and chamber pressure. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) was used to investigate the etching profile.

**PS-TuP3 Advanced Gate Stack Processes for sub-70nm CMOS Technology**, ***G.H. Kim***, *K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

The continued evolution of MOS (metal-oxide-semiconductor) transistor beyond the 90nm technology node will most likely be driven by advances in materials engineering and process integration. Fundamental changes in the materials used in the MOSFET (MOS field effect transistor) gate stack will become necessary as will novel processing techniques. High-k dielectrics can potentially extend scaling to thinner equivalent oxide thickness. However, in the production of very small size devices, the fine patterning technology is very important in order to manufacture the detailed device design based on the principle of the device operation. In this work, the dry etchings of new materials studied for the future CMOS devices are described. TiN as the metal gate electrode material and high-k gate insulators such as $HfO_2$ and $Al_2O_3$ are investigated. Etch rates and etch selectivity of TiN/high-k dielectrics gate-stack structures on Si substrate were investigated by varying the process parameters such as gas mixing ratio, source RF power, DC bias voltage, and process pressure. Plasma diagnostics were performed by quadrupole mass spectrometer (QMS) measurements and optical emission spectroscopy analysis. To investigate the etch residues of the high-K dielectric is generated by $BCl_3/Cl_2/O_2$ plasmas, the surface analysis on the dielectrics was performed using x-ray photoelectron spectroscopy (XPS).

**PS-TuP4 Etching Characteristics of High-k Dielectric Materials in Inductively Coupled $Ar/CF_4/C_4F_8$ Plasma**, ***S.W. Kim***, *B.J. Park*, Sungkyunkwan University, Korea, *S.-K. Kang*, SKKU Advanced Institute of Nano Technology, Korea, *K.S. Min, S.D. Park, G.Y. Yeom*, Sungkyunkwan University, Korea

For the next generation metal oxide semiconductor field effect transistor (MOSFET), high-k materials such as $HfO_2$, $ZrO_2$, BST, etc. are required as gate dielectric materials which replace $SiO_2/Si_3N_4$. To apply these high-k materials to the next generation devices, the etch characteristics needs to be satisfied in addition to the adequate materials characteristics. For these materials, precise etch rate is required instead of high etch rate due to the low thickness of the material and extremely high etch selectivity over underlayer material is required. Also, no damage or residue remaining on the etched surface is tolerable. In this study, the etch characteristics of high-k materials such as $HfO_2$ and $ZrO_2$ were investigated as a function of gas mixture composed of $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher, and the effect of gas mixture on the etch rate, etch selectivity to silicon, the remaining C-F polymer on the silicon surface, and the damage to the MOSFET device were investigated. In the presentation, the change of materials physical, chemical, and electrical properties etched by $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher will be shown in details with the properties of MOSFET devices fabricated by $Ar/CF_4/C_4F_8$ ICP.

**PS-TuP5 The Etching Mechanism of Zinc Oxide Thin Films for Optoelectronics Device Application using Inductively Coupled Plasma**, ***J.C. Woo***, *K.T. Kim, G.H. Kim, C.I. Kim*, Chung-Ang University, Korea

Zinc oxide (ZnO) exhibits an interesting combination of multifunctional properties, including optical, piezoelectric, and optoelectronic properties, and in thin film form ZnO films find immense applications in many electronic devices including sensors, transducers, and high frequency surface acoustic wave (SAW) devices. It has advantage relative to GaN because of its availability in bulk, single-crystal form, and wide bandgap energy of 3.4 eV, which makes it transparent to visible light. The excition binding energy is ~60 mV for ZnO, as compared to GaN, ~25meV; the higher excition binding energy enhances the luminescence efficiency of light emission. Research and development of ZnO have been rapidly accelerated to improve materials for the last decades. But, etch properties of ZnO have not established yet. Accordingly for many application optoelectronic devices, the etching mechanism of ZnO thin films during the etching process must be understood. However, few of etching mechanism was examined in our previous works and it can be hardly etched. So it is very important to improve the high etch rate, vertical etch profile, smooth etch surface, high mask selectivity and smooth sidewalls for developing ZnO thin films. In this study, we investigated etch characteristics of the ZnO thin films in the inductively coupled plasma system. The etching characteristics of ZnO thin films were investigated in terms of etch rates and selectivity as a function of additive gas mixing ratio. The plasmas were characterized by optical emission spectroscopy analysis and quadrupole mass spectrometer measurements. The chemical reaction on the surface of the etched ZnO thin film was investigated with X-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

**PS-TuP6 Study of the Amorphous Silicon Etching using Pin to Plate Dielectric Barrier Discharge in Atmospheric Pressure Plasma**, ***S.J. Kyung***, *J.B. Park, J.H. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

In this study, atmospheric pressure plasmas were generated with a modified dielectric barrier discharge (pin-to-plate DBD) having the power electrode composed of multi-pins instead of a conventional blank planar plate and their characteristics of discharge were investigated. The effect of $CF_4$ in the $N_2/NF_3$ gas mixture on the characteristics of the pin to plate dielectric barrier discharge (DBD) having the size of 170 x 100 mm have been investigated for the application to thin film transistor liquid crystal display (TFT-LCD) processing such as amorphous silicon(a:Si) and silicon nitride($Si_3N_4$) etching. The result showed that the selectivity of a:Si/ $Si_3N_4$) was increased with $CF_4$ flow rate in $N_2$/ $NF_3$ up to 250 sccm, however, the further increase of $CF_4$ flow rate decreased the selectivity of a:Si/ $Si_3N_4$). A maximum etch rate of a:Si of 110 nm/sec with the selectivity of a:Si/ $Si_3N_4$) of 5.1 could be obtained with a gas mixture of 250 sccm $CF_4$ in $N_2$ (50 slm)/ $NF_3$ (300 sccm) and at 8.5 kV of AC rms voltage.

**PS-TuP7 Effect of Gate Processing on Line edge Roughness in 45nm**, *P.K. Subramanian, **I. Matthew**, T. Wallow,* Advanced Micro Devices*, L. Tsou*, IBM Corporation

As gate lengths shrink in 45nm technology node and beyond, the variation contributed by Line Edge Roughness(LER) becomes a larger proportion of the total CD variation Therefore, a reduction in the LER is one way of reducing the total variability of gate dimensions across a chip. In this paper we study evolution of the LER through the various process steps that end with the formation of a gate on the wafer. We examine the frequency components of the roughness as the wafer processed through various (lithography and etch) steps and examine the effects of each of these processes on the roughness spectrum. The advent of the immersion lithography and the attendant higher Numerical Aperture(NA) has led to the adoption of new schemes to reduce reflectivity. The impact of the new lithographic schemes on LER evolution is also examined. We also examine the effects of modifying etch process parameters and chemistry on the roughness spectrum. The effect of HBr plasma curing during etch processing on the LER is studied.

**PS-TuP8 Directional Oxidation of Silicon Trench in Surface Wave Oxygen Negative Ion Plasma**, *H. Shindo, T. Mitomi, M. Suzuki, **K. Kusaba***, Tokai University, Japan

A low temperature and low damage silicon oxidation technique is highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. Additionally, a new type of MOS transistor with a trench gate has recently been proposed for the next generation of ULSI. For this purpose, a new method of negative ion assisted silicon oxidation has been proposed employing microwave oxygen plasmas. In this work, a new method of negative ion assisted silicon oxidation is proposed employing microwave oxygen plasma, and a directional and low temperature silicon trench oxidation will be demonstrated. The oxidation characteristics were intensively studied in silicon trench to form a shallow trench insulation layer for cell isolation of MOS transistor. The plasma was produced in an aluminum chamber 240 mm in diameter. At the one end of the chamber, a microwave of 2.45 GHz was introduced through a high permittivity material of AlN (permittivity: 10.9) window of disc plate. The oxidation characteristics were precisely examined in a silicon trench of 0.15 um width and 0.2 um depths. The oxidation was made in the condition of 400 degree C and the bias frequency of 1900 kHz. The oxidation depth at the three positions of the trench was determined from SEM photograph. These three positions are labeled as “Top, Side and Bottom” The oxidation depth at all positions was at first decreased with an increase in the axial distance from the microwave window, but it was increased again in the downstream. Particularly, the oxidation depth at the trench bottom showed a maximum in a very downstream of 18 cm from the window, and thus the step coverage of the trench oxidation, defined as the depth ratio of the trench bottom to the top, reached as high as 0.8. Since the axial distance at which the oxidation depth begins to increase again is just coincident with the region where the electron energy is rapidly decreased, this directional oxidation feature is ascribable to the negative oxygen ions. It is concluded that the oxidation by high density oxygen surface-wave plasma with high permittivity window is innovative.

**PS-TuP9 Dry Etching Technology of Cobalt Silicide for sub-60nm Gate Patterning using ICP Source with High Temperature ESC**, ***H. Lee***, Samsung Electronics, Korea*, J.I. Shin, H.S. Lee,* Applied Materials*, D.H. Kim*, Samsung Electronics, Korea*, T.W. Kim,* Applied Materials*, K. Shin, M.C. Kim, G.J. Min, C.J. Kang, J.T. Moon*, Samsung Electronics, Korea

Dry etching of $CoSi_2$ gate in sub-60nm design rule is successfully done using ICP (Inductively Coupled Plasma) source with high temperature ESC (Electro-Static Chuck). Vertical profile is achieved by forming a volatile Co byproduct reacted with $Cl_2$/Ar based plasma at 250°C of ESC temperature under relatively low DC bias voltage (~300V). Since $Cl_2$/Ar based plasma has low etch selectivity to polycrystalline Si (poly-Si) and gate oxide, $O_2$ and $N_2$ were added to reduce the recess of poly-Si layer which is remained beneath $CoSi_2$ layer during silicidation process. $CoSi_2$ layer used in this experiment was formed by sintering of sputtered Co layer on poly-Si layer. Dry etching of poly-Si is followed with both low temperature(~80°C) and high temperature (~250°C) ESC after $CoSi_2$ etching. For the poly-Si etching, $HBr/O_2$/He plasma was used to maintain high selectivity to gate oxide. However, even though poly-Si layer is recessed more than 200Å during $CoSi_2$ etching process, it was not possible to remove remaining poly-Si completely with $HBr/O_2$/He plasma. TEM and EDX are used to analyze surface of poly-Si, and thin metal layer containing Co is observed on the surface of polycrystalline Si layer. It is believed that this thin metal layer blocks etching of poly-Si. Therefore, removing the thin metal layer or preventing re-deposition of Co byproduct on polycrystalline Si layer during $CoSi_2$ etching will be necessary. Co as a barrier metal of bit line is also etched with vertical profile on high temperature (~300°C) ESC with $Cl_2$/Ar plasma. In this case, there was no remaining Co by-product since enough amount of Co OE is possible, resulting in complete removing of Co byproduct on ILD.

**PS-TuP10 Stripe and Hole Shape Contacts Etch for Power Amplifier BICMOS Devices**, ***J.P. Oddou***, *D. Ristoiu, J. Mourier*, STMicroelectronics, France

Power amplifier applications of BICMOS devices need a specific contact module in order to support high current density and temperature. In order to achieve such performances, stripe-shaped contacts are designed for the bipolar transistor, while classic hole contacts are used for CMOS and the contact depth is increased to 1.5µm. Therefore, taking into account the topography of the bipolar and MOS structures, 5 different types of contacts must be opened. To fulfill these specifications, contacts etch process requires: - sharp profile to achieve high depth contacts; - high selectivity of oxide to nitride to safely land on emitter, gate and active areas; - low loading effects to achieve both stripe and hole contacts having the same critical dimension (CD). In this paper we focus on oxide etch process for contact opening developed on a MERIE industrial etcher using C5F8/ O2/ Ar chemistries. In a first time we characterize the oxide to nitride selectivity and the profile slope as a function of the C5F8/O2 ratio. Higher C5F8/O2 ratio favors selectivity, but degrades slope and CD, while lower C5F8/O2 ratio leads to sharp profile in the detriment of selectivity, therefore our approach consists in using a sequence of etching steps having different C5F8/O2 ratio. We demonstrate that this process solution enables us to achieve the above mentioned morphological constraints. Moreover, electrical tests performed on contact chains show that the resistivity and leakage results are in line with technology specifications.

**PS-TuP11 Sidewall Passivation Effect during $C_4F_8$ + $N_2$ Etch Process for SiOCH Low-k Films**, ***S.-K. Yang***, *H.-S. Yoo,* Inha University, Korea*, H.-Y. Song,* Samsung Electro-Mechanics Co. LTD., Korea*, J.-G. Lee,* Bucheon College, Korea*, S.-G. Lee, B.-H. O, I.-H. Lee, S.-G. Park*, Inha University, Korea

Plasma induced damage to low k dielectric layer is one of key issues in developing the multi-level interconnection technology based on Copper and low k dielectrics. Change in chemical bonds and contents of carbon or fluoride often results in higher dielectric constant. In this work, etching of SiOCH low k films was studied by $C_4F_8$ + $N_2$ plasma in Inductively coupled plasma etcher. X-ray photoelectron spectroscopy showed C-F and C-N bondings on the sidewall of patterned low k dielectric layer, which indicated the formation of passivation film. This passivation layer remained after photoresist removal by $N_2$ plasma and even after dipping in 1% HF solution. It is shown that patterning of SiOCH layer by $C_4F_8$ + $N_2$ plasma caused the increase in dielectric constant k by forming C-F passivation films.

**PS-TuP12 Critical Dimension Shrink and Control with Different Frequency Source Powers in Dielectric Etch Chamber for 45nm Technology and Beyond**, ***J. Wang***, Applied Materials

The Critical Dimension (CD) shrink from BARC was invested by using the capacitive coupled plasma etcher with high frequency source due to BARC open step is the most critical in dielectric etch. Two frequencies (<100MHz vs >100 MHz) source power with different plasma densities were compared. It was found that the CD shrink was related to the CF2 species that were excited from source and>100 MHz source power showed the strong control knob on CD shrink comparing to <100MHz. Chemistry selection and process control knobs have been evaluated and it was found that the CD shrink was basically controlled by pressure, polymer gas, and source power. And a maximum >60nm CD shrink bias was obtained when profile and final CD range was maintained in the spec. (1) CD bias comparison on the BARC open with and without source power indicated source power strong effect on CD shrink. The CF2 radical emission in etching plasma were collected by the optical emission spectroscopy (OES) as shown to evaluate the difference on the CD shrink when other process parameters changed . It was found that the >100 MHz source provided the efficient generation of CF2 radical density that resulted in more CD shrink. The CD shrink varied with different source power for both frequencies and it showed the more CD shrinks with high source power. The CF2 species density without source power showed lowest signal and the strongest emission with the high source power, which was pretty much consistent with the wafer results. (2) CHF3 flow on BARC open was tested at different pressure and the high CHF3 gas flow and low pressure were showing strong knobs on CD shrink control with source power. It was known that CF2 was one of many species from CHF3 dissociation during the plasma etch and more CF2 has been generated with high frequency power, which deposited on the sidewall to protect the isotropic etch and therefore made the top CD shrink. With the low CHF3, the CD shrink range was much bigger than high CHF3 flow with pressure change. The CF2 species density explained why

high source power and low pressure as the knobs on CD shrink control. (3) The production-like runs on customerâ?Ts wafers were tested with two source powers and both showed CD shrink consistently repeatable. The high frequency source power provided the high plasma density as the strong knob for CD shrink and meantime allowed the high efficiency wafer-less dry clean, which benefited APF etch clean mode requirement.

**PS-TuP13 Analysis of High Aspect Ratio Contact Etch using High Flow Concept**, ***S.-J. Park***, *S.-C. Park, Y.-J. Kim, W.-S. Han*, Samsung Electronics Co. Ltd., Korea

As contact sizes scale down below 100nm, high aspect ratio contacts (HARC) encounter the limits such as the low selectivity of the resist material, etch stopping mechanism, the profile distortion, and so on. The high flow concept is a widely used scheme for RIE (reactive ion etching) technology. The rapid movement of reactive ion sources affect on the dissociation mechanism of the etching chemistry. The carbofluoride (CxFy) chemical sources show different behaviors, while the flow rate changes at the same pressure. The QMS (quadrapole mass spectroscopy) method enables the analysis of the dissociated chemicals and the byproducts during HARC etch. The ratio of carbofluoride and fluorine seem to be the major factor which determines the profile of HARCs and the resist selectivity. The contact patterns with an aspect ratio of 30 are used to identify the high flow concept in this experiment. The flow rate of carbofluoride chemistry changed up to 2.8 times higher than the normal reference flow rate in a CCP (capatively coupled plasma) chamber. The higher flow rate improves in terms of the resist selectivity. However, the profile distortion between the top opening and the bottom opening is worse than the profiles under the normal condition. The HARC etch study at the high flow condition will be shown in terms of the profile distortion and the real time chemistry monitoring using QMS method.

Keywords : RIE, HARC, high flow.

**PS-TuP14 Improvement of Sputter Deposited Mo-based Barrier Films by Insertion of a Thin Al Interlayer for Copper Metallization**, ***P. Majumder***, *C.G. Takoudis*, University of Illinois at Chicago

Copper is used as interconnects in advanced ultra large scale integration microelectronic devices due to its low electrical resistivity and superior resistance to electromigration compare to Al. However, Cu diffuses easily into Si and $SiO_2$, and forms copper silicide compounds at temperatures as low as 200 °C, resulting in degradation of Si devices at low temperature. Therefore, the use of diffusion barriers between Cu and Si becomes essential in order to successfully implement copper as an interconnecting metal. Sputter-deposited refractory metals, like W, Ta, Mo, and Ti and their nitrides have been recognized as diffusion barriers due to their high thermal stability, low resistivity and excellent capability of suppressing reactions between Cu and Si. In recent years, Mo-based diffusion barriers have been investigated for copper metallization. Many studies show that sputtered deposited Mo and $MoN_x$ barrier layers are polycrystalline in nature and thus failed after annealing at relatively lower temperatures due to the diffusion of copper through the grain boundaries of the polycrystalline films. In this work, we investigate the barrier performance of sputtered deposited Mo and $MoN_x$ due to the insertion of ultrathin Al interlayer. Al is used to stuff the grain boundaries of Mo and $MoN_x$ thereby increasing the breakdown temperature of the barrier films. Mo and $MoN_x$ films are sputtered deposited using Ar and $Ar/N_2$ mixture, respectively, under a 4.5 mtorr total sputtering pressure. The formation of crystallites takes place on the surface of the copper layer at the barrier failure temperature. The quantitative analysis of these crystallites is done using energy-dispersive spectroscopy. The thermal stability of Mo-based barrier layers are evaluated after annealing at wide range of temperatures in the presence of $N_2$ using four probe measurements for sheet resistance, X-ray diffraction analysis for phase identification and scanning electron microscopy for surface morphology. The interaction of different layers due to high temperature annealing is evaluated by depth profiling using X-ray photoelectron spectroscopy.

**PS-TuP15 Ar Ion and Ammonia Modification of OSG Surfaces: A Novel Route to Nanoscale Diffusion Barriers**, *J. Wilks*, ***J.A. Kelber***, University of North Texas

The continued scaling of barriers to < 4 nm thickness drives the quest for a practical single step deposition process, in contrast to the current TaN/Ta two step standard. Pure Ta deposition has been considered, but Ta deposition on OSG and related materials results in a Ta-O-C "interphase" 2-4 nm thick which inhibits Cu adhesion and prevents barrier scaling to sub-4 nm length scales. We present in-situ XPS and ex-situ AFM data indicating that 500 eV Ar ion bombardment in the presence of ammonia results in a self-limiting process involving carbon depletion and nitrogen addition to the surface region. No significant change in surface rougness is observed. The surface nitridation results in a qualitatively different response to Ta deposition: an abrupt interface with initial Ta2N formation, with subsequent Ta formation at longer deposition times. These results suggest a new direction in plasma pretreatment of OSG surfaces prior to metallization--a self-limiting surface nitridation, followed by a single step Ta PVD process resulting in a Ta2N/Ta nanoscale barrier. Further, the results observed for the ion bombardment process mimic in major respects results observed for low pressure plasma treatments--including enhanced carbon depletion due to the presence of ammonia, the self-limiting nature of the process, and nitrogen incorporation. The usefulness of such UHV-based processes as models for low-pressure plasma processing will also be discussed.

**PS-TuP16 Size Distribution Factor of Platinum Nanoparticles Synthesized by Plasma in Aqueous Solution**, ***T. Nishigaki***, *T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

Well-defined platinum nanoparticles activate of photo catalysis, decompose harmful component in exhaust gas of automobile, lead to high potential of fuel cell. Platinum nanoparticles have been synthesized by various techniques including chemical reduction, photo reduction and electrochemical technique. However, in these techniques, it takes few hours to synthesize the nanoparticles or chemically toxic substances leave in a product. Now, it is required to develop a green process rapidly to synthesize nanoparticles. We have developed 'Solution Plasma', which is defined as plasma in aqueous solution. Solution plasma has attracted much attention as a novel chemical reaction field. As solution plasma generates UV light, electrons, and radicals, higher reaction rate would be achieved. In this study, we aimed to synthesize platinum nanoparticles by solution plasma. In addition, we investigated influence of solution pH on the sizes of the platinum nanoparticles. Optical absorption of nanocolloidal platinum was measured by UV-vis spectrometer. The nanoparticles were observed by transmission electron microscopy (TEM). $H_2PtCl_6?6H_2O$ (1.44mM) and PVP (Polyvinylpyrrolidone, 12.1mM) were used as row materials. The pH of solution was varied from 2.5 to 4.5. The electrical conductivity was adjusted to 1.5mS/cm by the addition of KCl. A pulsed power supply was utilized to generate plasma. Pulsed voltage of 1.6kV was applied between the tungsten electrodes in the solution. Pulse width and frequency were varied from 2.0 to 3.0μs, respectively. Solution color changed from orange to dark brown at discharge times of more than 40 min. An absorption peak at 262 nm originated from $PtCl_6^{2-}$ became weaker with the increases of the discharge time, while baselines in the spectra became higher in all the range. These results indicate the formation of platinum particles. TEM image shows that the mean diameter of the nanoparticles was 10nm. Debye rings by (111), (200), (220), (311) were also observed by diffraction patterns. The effects of pulse width, frequency and pH on the particle size distribution were also discussed.

**PS-TuP17 Effects of Ions and Radicals on the Growth of Single-Walled Carbon Nanotubes Produced by Diffusion-Plasma CVD**, ***T. Kato***, *R. Hatakeyama*, Tohoku University, Japan

Individual single-walled carbon nanotubes (SWNTs) have attracted a great deal of attentions since the discoveries of their prominent electrical and optical characteristics. Recent progresses in a synthesis stage of the isolated SWNTs provide outstanding opportunities to efficiently study the basic science of ideal one-dimensional materials. A plasma CVD is well-known as a nanotube formation method including outstanding benefits in the vertical growth of individual multi-walled carbon nanotubes. Up to now, our group firstly demonstrated that those benefits in the plasma CVD can be also applied to the SWNT growth stage, and the freestanding individual SWNT growth on a flat substrate has been achieved with a diffusion plasma CVD method. These progresses of a plasma technology in the nanotube fabrication field can strongly accelerate industrial application of SWNTs. Unfortunately, however, any quantitative discussion about effects of plasmas on the growth of SWNT has not been realized at all so far, and it is one of inevitable issues to fully utilize potential abilities of plasmas for a realistic use of SWNT-device applications. These backgrounds motivate us to investigate the detailed effects of plasmas on the growth of SWNTs. In our study, the effects of ion energy and radicals are mainly focused with a precisely parameter- controlled diffusion plasma CVD system. Derived from the carefully investigated experimental results about the time evolution of SWNT growth, the simple equation is established to describe the growth kinetics of SWNTs during the plasma CVD. Based on the fitting of the experimental result with the equation, remarkable effects of ions and radicals are uncovered. There are clear threshold energies of ions for the destruction of the tube structure. It is conjectured that those threshold energies correspond to that of the bond breaking between carbon in the nanotube and the displacement of the carbon atom from a graphite network in the nanotube. In the case of the radicals, the etching rate during the SWNT growth is found to be strongly influenced by the amount of atomic hydrogen in the plasma. Furthermore, a unique correlation is also identified between the incubation time of the SWNT growth and density of ions in the plasma. These discoveries of the interesting correlations between the

detailed growth parameters of SWNTs and key elements in plasmas could contribute to the further advance for the perfect structure control of SWNTs.

**PS-TuP18 Structure and Properties of Tungsten Carbide / Amorphous Hydrogenated Carbon Composite Films Prepared by Plasma Immersion Ion Immersion and Deposition**, *M. Xu,* Shanghai Jiaotong University and City University of Hong Kong, *Z.W. Wu, S.H. Pu,* City University of Hong Kong, *X. Cai,* Shanghai Jiaotong University, Hong Kong, ***P.K. Chu***, City University of Hong Kong

Amorphous carbon films have excellent properties including high hardness, low friction coefficient, high chemical inertness, and good corrosion resistance. Metal-containing hydrogenated carbon films have recently attracted attention as nanocomposite films with microstructures comprising nanocrystalline grains in an amorphous matrix. These composite films have properties intermediate between a-C:H films and metal carbides and their mechanical and tribological properties and suitable for some applications. A variety of methods such as plasma-assisted chemical vapor deposition (CVD), magnetron sputtering and ion beam assisted deposition (IBAD) have been developed to produce MeC/a-C:H films. Acetylene (C2H2) plasma ion immersion implantation and deposition (PIII&D) was used in this work to fabricate carbon films with better adhesion to the substrate. Tungsten ion implantation was subsequently conducted without breaking vacuum to produce WC/a-C:H films in which there is a gradual transition region between the WC and a-C:H. The composition and structure of the films were evaluated by X-ray photoelectron spectroscopy and glancing angle X-ray diffraction. High resolution transmission microcopy was adopted to investigate the structure transformation. The surface morphology was observed by atomic force microscope and the hardness by nanoindentation measurements. Our results indicate that in addition to the formation of WC nanocrystalline grains in the amorphous structure, high energy W ion implantation reduces the sp2 contents and consequently enhancesm the mechanical properties.

**PS-TuP20 Effect of Multi-polar Magnetic Field on Properties of Nano-crystalline Silicon Thin Film Deposited by Large-area Internal ICP-PECVD**, ***H.B. Kim***, *H.C. Lee, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Nano-crystalline silicon films have broadly been studied due to their applications to the thin-film-silicon solar cells and the TFT(Thin Film transistor) for the elimination of light induced degradation, the enhancement of long wave length response, and high electric mobility by comparison to amorphous silicon films. Especially, the deposition of nano-crystalline with a high deposition rate at the low temperature below 200°C is important. In other to realize the nano-crystalline silicon at a low temperature, a high density plasma such as inductively coupled plasma (ICP) is required. The conventional high density plasma sources have mainly been focused on the external ICP types, however, these sources show some problems in extending to a large area due to the very thick dielectric windows and standing wave effect. On the other hand, the use of an internal type antenna where the ICP antenna is inserted into the plasma gives more feasibility in depositing nano-crystalline silicon on the large area uniformly. And the application of multi-polar magnetic field is believed to improve the properties of the deposited film. In this study, as an internal type large-area plasma source, U-type internal linear ICP source using multi-polar magnetic field utilized to deposit nano-crystalline silicon on the glass substrate (370mm x 470mm) at the temperature below 200°C using $H_2/SiH_4$. ICP power of 13.56 MHz is in the rage of 100 W - 4000 W and the working pressure was varied from 10 to 60 mTorr. In this presentation, the variation of physical, chemical, and electrical properties of the nano-crystalline silicon deposited by the large area internal ICP with multi-polar magnetic field will be presented as compared to the source without multi-polar magnetic field.

**PS-TuP21 Study on Plasma Assisted Metal-Organic Chemical Vapor Deposition of Ti(C,N) and Zr(C,N) Thin Films and In-Situ Plasma Diagnostics with Optical Emission Spectroscopy**, *J.-H. Boo, C.-K. Jung, D.C. Lim, M.C. Kim,* ***S.J. Cho,*** *J.G. Han*, Sungkyunkwan University, Korea

Ti(C,N), Zr(C,N) films were synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. $H_2$ and $He+H_2$ gases were used as the carrier gases to compare plasma parameter. The effect of $N_2$ and $NH_3$ gases as reactive gas was also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma were analyzed by optical emission spectroscopy (OES) at various pulsed bias and gas conditions. He and $H_2$ mixture as carrier gas was very effective in enhancing ionization of radicals, especially $N_2$ resulting is high hardness. However, $NH_3$ as reactive gas highly reduced the formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species and bias voltage. Higher hardness can be obtained for $H_2$ and $N_2$ gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using $N_2$ gas prior to deposition appeared to increase adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

Keywords: Ti(C,N) and Zr(C,N) films, Low temperature pulse DC-PAMOCVD, Optical emission spectroscopy, High hardness

## Plasma Science and Technology

## Room: 606 - Session PS1+NS-WeM

## Plasmas in Nanotechnology

**Moderator:** S. Kodambaka, University of California, Los Angeles

8:00am **PS1+NS-WeM1 Spectroscopic, Spatial, and Temporal Investigation of Fe Nanoparticle Synthesis by Through Thin Film Ablation**, ***A.R. Waite***, University of Dayton, Air Force Research Laboratory and UTC, Inc., *P.T. Murray*, University of Dayton, *J.G. Jones*, Air Force Research Laboratory, *E. Shin*, University of Dayton, *A.A. Voevodin*, Air Force Research Laboratory

Nanoparticles of Fe have been formed by the process of Through Thin Film Ablation (TTFA). In the TTFA process, the target consists of a thin film (10-20 nm thick) of material that has been applied to an optically transparent support. The thin film target is ablated in vacuum through the transparent support, and this produces a directional plume of nanoparticles. Optical Emission Spectroscopy (OES), Time-of-Flight (TOF) analysis, and high-speed Intensified Charge Coupled Device (ICCD) imaging are utilized to study the plume dynamics and characteristics. OES measurements indicate the ejected nanoparticles to have a temperature of 2232 K, suggesting they are liquid. TOF analysis indicated that there are two main size constituents in the ablation plume, higher speed atomic species and slower nanoparticles. ICCD imaging is used to further study the plume dynamics in both time and space. Ablation in vacuum and in the presence of a background gas will be discussed.

8:20am **PS1+NS-WeM2 Size Manipulation and Control of Nanoparticles Produced from Atmospheric-Pressure Microplasmas**, ***N.A. Brunelli***, *K.P. Giapis*, California Institute of Technology

Size manipulation and control of nanoparticles produced from atmospheric-pressure microplasmas Atmospheric-pressure microdischarges have been shown to produce silicon nanoparticles between 1-2 nm in diameter, which exhibit intense photoluminescence emission at 420 nm with quantum efficiency of 30%.[1] For imaging applications, it is desirable to have an emission at longer wavelengths which requires larger diameter 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 the combination of a microdischarge with a CVD reactor can overcome this problem by achieving overgrowth of the seed particles produced in the microdischarge. For example, silicon nanoparticles can be enlarged from 2.5 nm to 3.5, 4.5 and 5 nm by mixing an additional 150, 300 and 600 ppm of sila4ne in argon, respectively. In fact, the CVD overgrowth allows not only tuning of the particle size but also permits selection of an alternate overgrowth layer, creating core-shell structures. Examples of Ge and Fe cores overgrown with Si will be shown. We quantify this claim by using a new ultrafine radial differential mobility analyzer immediately after the furnace to monitor in real-time the particle size. We characterize the nanoparticles by AFM, photoluminescence (PL) spectroscopy and transmission electron microscopy. As oxidation has been shown to affect the PL emission,[2] we have encapsulated the particles in thin films to ensure observed light emission is from radiative recombination. Beyond enlarging the seed particle diameter, we demonstrate the synthesis of core-shell structures consisting of an inexpensive metallic core and a thin overlayer of catalytically active material as the shell. Electrochemical measurements demonstrate the catalytic activity and performance of Fe-Pt and Co-Pt core-shell nanoparticles for fuel cell type applications.

[1] Sankaran, R. M., D. Holunga, et al. (2005). "Synthesis of blue luminescent Si nanoparticles using atmospheric-pressure microdischarges." Nano Letters 5(3): 537-541.

[2] Biteen, J. S., N. S. Lewis, et al. (2004). "Size-dependent oxygen-related electronic states in silicon nanocrystals." Applied Physics Letters 84(26): 5389-5391.

8:40am **PS1+NS-WeM3 Ionic Plasmas Yielding Novel-Structured and -Functional Nanocarbons**, ***R. Hatakeyama***, *T. Kaneko, W. Oohara, Y.F. Li*, Tohoku University, Japan **INVITED**

Nanocarbons of carbon allotropes have attracted a great deal of attention due to their high potential for novel properties and a variety of applications. Since fullerenes and carbon nanotubes among them are furnished with hollow inner nanospaces, it is a fascinating challenge to inject various kinds of atoms and molecules into the nanospaces based on plasma nanotechnology, which could lead to innovative functionalization of the pristine ones. For that purpose original approaches using nanoscopic plasma processing mainly in ionic plasmas have been performed in order to develop fullerene-, SWNT(single-walled carbon nanotube)- and DWNT(double-walled carbon nanotube)-based materials with new functions corresponding to electronic and biological appilications. Firstly, the encapsulation of charge-exploited alkali atoms inside the fullerene is realized ($Li@C_{60}$ etc.) using alkali-fullerene plasmas as ionic plasmas, which consist of positive alkali ions and negative $C_{60}$ ions. Then the atomic nitrogen as a spin-exploited atom is also encapsulated inside $C_{60}$ ($N@C_{60}$). In relation to the inner nanospace modification of the carbon nanotubes, another ionic plasmas, i.e., alkali-halogen plasma and pair-ion plasma are generated, which consist of positive alkali ions and negative halogen ions, and positive-$C_{60}$ and negative-$C_{60}$ ions with an equal mass, respectively. Furthermore, an electrolyte solution plasma including DNA negative ions is prepared. The substrate bias method is utilized mainly in these plasmas, where positive and negative ions with their energies and fluxes controlled are irradiated to an immersed substrate coated with the pristine carbon nanotubes . In addition, a thermal and plasma combined process is also devised for the treatment of both charge- and spin-exploited atoms. Consequently, we have innovatively created alkali-metals encapsulated SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs), halogen-elements encapsulated SWNTs (I@SWNTs), ferromagnetic-atoms encapsulated SWNTs (Fe@SWNTs), fullerene molecules encapsulated SWNTs and DWNTs ($C_{60}$@SWNTs, $C_{60}$@DWNTs, $C_{70}$@DWNTs, $C_{84}$@DWNTs), and DNA molecules encapsulated SWNTs (DNA@SWNTs) . Finally, their electronic and magnetic properties are intensively investigated. As a result, we have for the first time succeeded in realizing the continuous transition of air stable electronic transport from p-type to n- type semiconducting property by adjusting an amount of dosed atoms and molecules inside SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs, I@SWNTs, $C_{60}$@SWNTs, $C_{60}$@DWNTs), and in forming nano structures of magnetic semiconductor (Fe@SWNTs), nano pn junctions with rectifying characteristic [(Cs/I)@SWNTs)], and nano structures with distinct negative differential resistance of high peak-to-valley ratio ($C_{60}$@DWNTs, $C_{70}$@DWNTs, $C_{84}$@DWNTs) . In the case of DNA@SWNTs an experimental system utilizing an interfacial region between the gas and liquid phases has been constructed in order to enhance the DNA encapsulation rate. Here an ionic liquid consisting of only positive and negative molecules is introduced into the liquid phase, which can be regarded as an ionic plasma, i.e., fully ionized electrolyte plasma.

9:20am **PS1+NS-WeM5 Continuous-Flow Microplasma Synthesis of Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang*, ***R.M. Sankaran***, Case Western Reserve University

Carbon nanotubes (CNTs) have been synthesized in a continuous-flow, gas-phase catalytic process. The synthesis technique consists of two steps: 1) production of well-defined metal nanoparticles in an atmospheric-pressure microplasma and 2) catalytic growth of carbon nanotubes in a tube furnace reactor. In the first step, nanoparticles are generated using a direct-current (dc) hollow cathode microplasma made-up of a stainless steel cathode with a pin-hole (d~180 μm) and an arbitrarily-shaped tube anode. Gaseous precursors are introduced into the microplasma at atmospheric-pressure and decomposed non-thermally by electron impact to generate reactive radical species. Under appropriate precursor saturation conditions, the radicals polymerize to nucleate particles homogenously in the gas phase. Particle growth is limited to the small reactor volume (less than 1 nL) created by the microplasma geometry. As a result of the large concentration gradients and short residence time, the technique is capable of producing very small (1-3 nm diameter) nanoparticles with narrow size distributions. The particle-laden flow is then continuously fed to a second reactor to grow carbon nanotubes in free flight with addition of acetylene and hydrogen and heating at fixed temperatures between 500 and 1000 $^{o}$C. Nanotube size and distribution are determined on line using a gas-phase electrophoretic mobility macromolecular analyzer (GEMMA). In situ aerosol classification allows experimental conditions to be directly related to growth parameters. We have recently investigated the catalytic properties of iron and nickel nanoparticles toward growth of carbon nanotubes. Process parameters were optimized to prevent amorphous carbon formation and obtain high-quality CNTs. Ex-situ techniques such as Raman spectroscopy and transmission electron microscope (TEM) were used to characterize the structure of the carbon nanotubes. The combination of continuous-flow synthesis using microplasmas and the GEMMA system opens new possibilities for nanocatalyst synthesis and provides a methodology for enhancing our fundamental understanding of catalytic behavior.

9:40am **PS1+NS-WeM6 Low Temperature Growth of Single-Walled Carbon Nanotubes by Oxygen-Assisted Inductively Coupled Plasma Chemical Vapor Deposition**, ***C.-H. Hsiao***, *C.-H. Weng, Z.-Y. Juang, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with $CH_4/H_2$ gas mixture as base processing gases. A unique $Ni/Al/SiO_2$ nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. Parametric experiments were conducted to optimize the $O_2$ fraction in the gas mixture. The SWNTs were successfully synthesized at a temperature as low as 600°C.

10:40am **PS1+NS-WeM9 Fabrication of Defect-Free and Diameter-Controlled Silicon Nanodisks for Future Quantum Devices by using Neutral Beam Etching**, *T. Hashimoto,* ***T. Kubota***, *C.H. Huang,* Tohoku Univ., Japan, *M. Takeguchi,* National Inst. for Mtls Sci., Japan, *K. Nishioka,* Japan Adv. Inst. of Sci. and Tech., *Y. Uraoka, T. Fuyuki,* Nara Inst. of Sci. and Tech., Japan, *I. Yamashita,* Matsushita Electric Industrial Co., Ltd, Japan, *S. Samukawa*, Tohoku Univ., Japan

Nanometer-scale structures, such as quantum dots, are widely studied because of their possible application in the development of quantum-effect devices, such as quantum-dot lasers and single-electron transistors. To develop practical and robust quantum-effect devices, manufacturers must be able to fabricate selectively arranged, defect-free, sub-10-nm-scale structures of uniform size on substrates. To realize a nanometer-scale structure, we used a ferritin iron core (7 nm in diameter) as a uniform and high-density template and our developed neutral beam (NB) etching process for damage-free etching. We fabricated a "nanodisk,"a nanometer-thick disk-shaped silicon structure by patterning <3.5-nm poly-Si layer / 1.4-nm $SiO_2$ layer / Si substrate> by using NB etching with a ferritin iron-core mask. To precisely control the diameter of the nanodisk, we must selectively remove the surface native silicon oxide layer before Cl neutral beam etching because the Cl neutral beam has extremely high selectivity to $SiO_2$ film. SEM and TEM observations revealed that the nanodisk was successfully fabricated and that the buried $SiO_2$ layer was not damaged during etching. When the nanodisk was only etched by using the Cl neutral beam with the iron core mask, the diameter of the nanodisk was about 13 nm. To shrink the diameter of nanodisk, we developed a dry process to remove native oxide by using $NF_3$ gas and hydrogen radicals ("$NF_3$ treatment"). By using the $NF_3$ treatment to remove the native oxide, we decreased the nanodisk diameter to 10 nm. We found that removing the surface native oxide is very important for controlling the diameter of nanodisk. We then measured the I-V characteristics by using atomic force microscopy (AFM) with a conducting probe. Coulomb staircases were observed from the I-V measurements of the nanodisks at 25 K and at room temperature. These results indicate that the nanodisks we fabricated have a precise quantum-effect structure, and they attained single-electron properties. This research has great potential in the development of practical and robust fabrication processes for future quantum-effect devices. A part of this work was supported by the Nanotechnology Support Project and the Leading Project of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

11:00am **PS1+NS-WeM10 Parallel Writing of Complex Nanofeatures using Nanopantography**, ***L. Xu***, *A. Nasrullah, M. Jain, Z. Chen, V.M. Donnelly, D.J. Economou, P. Ruchhoeft*, University of Houston

Nanopantography is a technique for massively parallel writing of nano-sized features. A broad-area, collimated, monoenergetic ion beam is directed to an array of sub-micron-diameter electrostatic lenses fabricated on a conductive substrate (e.g., doped Si wafer). By applying appropriate voltages to the lens electrodes, each "beamlet" entering the lens is focused to a spot on the wafer surface. The spot size can be up to 100X smaller than the diameter of the lens. With the choice of an $Ar^+$ beam in the presence of $Cl_2$ gas, 10 nm-dia holes were etched in Si; while with the choice of a $Ni^+$ beam, ~10 nm nickel dots were deposited on Si. Nanopantography has the capability to write arbitrary nano-sized features since the focal points can be displaced by tilting the substrate. A second-generation nanopantographic system was built to allow writing of complex nano-features. The improved system design had an ion flux ~ 15X higher than the first generation reactor. A LabView-controlled motorized stage could be tilted in both the X- and Y-axes with an accuracy of 0.011° degrees. This corresponds to translation of the focal point by 1.5 nm on the substrate. The energy distribution of the extracted ion beam was measured to have a spread of 2.2 eV, for a 100 eV beam. By continuously tilting the substrate in one direction, nanotrenches with ~15 nm (FWHM) width and ~40 nm depth were etched in a Si wafer. More complex patterns, such as letters of the alphabet, were also etched into Si in a massively parallel fashion by two-dimensional tilting of the substrate.

11:20am **PS1+NS-WeM11 High Aspect Ratio Deep Trench Chamber and Process Development for Silicon Etch in DRAM Applications below 50 nm**, ***S. Wege,*** *S. Barth,* Qimonda Dresden, Germany, *A. Kersch,* Qimonda Munich, Germany, *M. Reinicke,* Dresden University of Technology, Germany, *G. Wenig,* Qimonda Munich, Germany, *M. Rudolph, J. Sobe, A. Steinbach*, Qimonda Dresden, Germany

For QimondaÂ´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 50nm. In this paper we describe the development of advanced DT plasma etch chamber and process to fulfill these requirements. New process regimes, e.g., RF pulsing and high temperature showed promising results. Simulations were combined with in-situ plasma measurement techniques, e.g., QMS with ion energy analysis, high resolution OES, insitu IR absorption spectroscopy, 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 with RF pulsing. The optimization of the side wall passivation stoichiometry is a key for high aspect ratio silicon etch. In addition, the etch process chamber includes new features for process control, in-situ wafer surface temperature and trench depth measurement. The equipment and process development was accomplished through close cooperation between Qimonda and the tool supplier.

11:40am **PS1+NS-WeM12 Etch Selectivity and Surface Roughening of Polystyrene and Poly(methyl methacrylate) in Plasma Etching of Block Copolymers**, ***Y.-H. Ting***, *S.-M. Park, C.-C. Liu, X. Liu, F.J. Himpsel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Polystyrene -block-poly(methyl methacrylate), (PS-b-PMMA) diblock copolymers are a promising lithography alternative for nanometer scale features. The two components segregate into nanoscale domains when the polymer solution is spun on to form a thin film and annealed above the glass transition temperatures of both components. Preferential removal of PMMA domains through plasma etching to leave behind a PS mask for subsequent etching of underlying layers is the focus of this work. The quality of the PS mask is characterized by the thickness and lateral dimension of the PS structures after removal of the PMMA, as well as the smoothness of its surfaces. We have characterized the effects of different plasma chemistries including O2, Ar/O2, Ar, CF4 and CHF3/O2 on etch selectivity and surface/sidewall roughness for PS and PMMA. The surface roughness of PS and PMMA after Ar/O2 plasma etching (which gave the best overall etch performance) was further examined as a function of ion bombardment energy to understand the roughening mechanisms, as the two polymers show different responses to changing plasma conditions. Specifically, the surface roughness of PMMA increases with increasing ion bombardment energy, while that of PS decreases. An oxidation-induced micro-masking process on PS surfaces upon plasma exposure has been proposed to explain the different in roughening of PS and PMMA. Surface chemical analysis using NEXAFS shows that chemical change occurs on the PS surface during exposure to oxygen containing plasmas. Evidence of inhomogeneities in the composition of the PS film suggests that surface inhomogeneities in chemical composition may persist and change chemically upon plasma exposure. Variations in etch resistance associated with the inhomogeneities may in turn be responsible for observed surface roughness. Roughening caused by this "micro-masking" effect is reduced under conditions that minimize selectivity, such as high ion bombardment energies. We acknowledge support from the UW NSF MRSEC for Nanostructured Materials.

12:00pm **PS1+NS-WeM13 Comparison between $NF_3$ and $CF_4$ Chemistries for the Selective Etching of SiGe Sacrificial Layers in a 300mm Chemical Dry Etching Reactor**, ***S. Borel***, CEA-Leti MINATEC, France, *C. Arvet,* STMicroelectronics, *D. Watanabe*, Shibaura Mechatronics Corporation, Japan

The selective removal of a SiGe sacrificial layer is a key step in the realization of several architectures that are based on the SON technology.

Such a process has been developed and studied in 200mm, showing very good results in terms of selectivity by using $CF_4$ as an etching gas. This competence has been transferred in 300mm by using a new generation chemical dry etching tool that offers an additional and alternative source of fluorine which consists in $NF_3$. A process based on this environment-friendly molecule has been developed and compared with the $CF_4$ reference in terms of SiGe:Si selectivity while keeping a comparable etch rate. In that aim, a strong dilution (1:10) was necessary because of the high dissociation level of $NF_3$ that results in high etch rates. Morphological analyses clearly show that the selectivity obtained by using $NF_3$ is prohibitive for the realization of advanced devices. Indeed, the selectivity value is around 3, which means that the thinning of the Si cap is only 3 times lower than the SiGe tunnel depth whereas it needs to be higher than 30 (it reaches 70 by using $CF_4$). Surface analyses by XPS reveal that a Si substrate exposed to the $CF_4$ process presents some carbon, which suggests a passivation mechanism that may be involved in the selectivity. With the carbon-free $NF_3$ molecule, this phenomenon does not occur, hence the lack of selectivity we observe. As a conclusion, even if it is possible to etch SiGe faster than Si by using $NF_3$, the reference process made of $CF_4$ remains the best solution for the tunnel etching of advanced devices where a controlled etch rate is necessary and a high SiGe:Si selectivity is mandatory.

## Plasma Science and Technology

## Room: 607 - Session PS2-WeM

## Plasma-Surface Interactions I

**Moderator:** J.P. Chang, University of California at Los Angeles

8:00am **PS2-WeM1 Measurement of Electron Shading and its Depletion by Ultraviolet Radiation using Scanning Surface Potential Microscopy**[1], *G.S. Upadhyaya, **J.L. Shohet**,* University of Wisconsin-Madison, *J.B. Kruger*, Stanford University

Electron Shading, or topography-dependent charging, is believed to occur during plasma exposure when the depth-to-diameter ratio (aspect ratio) of pattern features is greater than 0.5. We present preliminary direct experimental evidence of the existence of electron shading. In addition, we present evidence of removal of the electron shading by exposure of the charged structure to UV radiation produced by a Hg-Ar lamp A patterned test structure was exposed to a d.c. nitrogen plasma operating at a pressure of 120 mTorr. The pattern was composed of a layer of thermally grown oxide with circular pits of 800 nm diameter and 1 micron depth. The pit pitch was 1.6 microns. The structure was placed on the cathode of the discharge to which -500 V was applied to break down the gas and to bombard the surface with ions. The structure was exposed to the plasma for a total of 10 seconds. A Digital Instruments multimode Atomic Force Microscope was modified to operate as a Kelvin probe in order to measure the surface potentials with sufficient spatial resolution to determine the potential inside the pit regions. To enhance the resolution beyond the standard AFM tip dimensions a carbon nanotube was attached to the apex of the AFM tip. Three two dimensional surface potential scans were made. First, a scan of the unexposed test structure showed that the surface potential was less than 10 mV over the surface of the unexposed structure. After plasma exposure, a second scan showed d.c. surface potential of the order of 6 volts over the entire structure. In addition, higher potentials (of the order of 200 mV) were observed directly over the pit regions, thus showing that electron shading appears to be present. The third scan (after UV exposure) shows removal of all surface potentials inside and out of the pit region and returns the structure to the uncharged state before plasma exposure.

[1] Work Supported by NSF under grant DMR-036582 and under grant ECS-9731293.

8:20am **PS2-WeM2 Surface Reaction Enhancement by UV Irradiation during Si Etching with Chlorine Atom Beam**, ***B. Jinnai***, Tohoku University, Japan, *F. Oda, Y. Morimoto,* Ushio Inc., Japan, *S. Samukawa*, Tohoku University, Japan

The surface atomic layer chemical reactions must be accurately controlled in future nanometer scale ULSI devices to enable precise patterning without any irradiation damage being caused during plasma etching processes. Many investigations have been conducted to understand surface reactions during silicon etching in chlorine plasma. Such research has focused on the effects of energetic ion and radical species using high-energy ion beam experiments. However, we recently found that the UV photon irradiation from plasma also plays a very important role in surface reactions during silicon etching in chlorine plasma. In this study, we discuss the effects of UV photon irradiation from chlorine plasma during silicon etching with our developed low-energy chlorine atom beam. A silicon substrate was etched by combining a low-energy chlorine atom beam and UV photon irradiation. When the silicon substrate was irradiated to the UV photons from 200 nm to 380 nm during etching with the chlorine atom beam, the etching rate of silicon was drastically increased. The results suggest that UV photons with wavelengths between 200 nm to 380 nm enhance the silicon surface reactions in the chlorine plasma. Additionally, a total photon irradiation density must be greater than 20 $mW/cm^2$ to increase the etching rate of silicon. Namely, the silicon surface reactions strongly depend on the wavelength (the energy) of the UV photons and the UV photon flux in the chlorine plasma. Our results are the first to clarify that UV photon irradiation from plasma plays very important roles in silicon surface atomic layer reactions in chlorine plasma.

8:40am **PS2-WeM3 Vacuum-Ultraviolet Radiation-Induced Charge Depletion in Plasma-Charged SiO2/Si by Electron Photoinjection and Fowler-Nordheim Tunneling**[1], ***G.S. Upadhyaya**, J.L. Shohet*, University of Wisconsin-Madison

Vacuum-ultraviolet (VUV) radiation emitted from processing plasmas can damage dielectric materials by creating electron-hole pairs. However, the resulting increased dielectric conductivity during VUV irradiation can also be beneficial in either partially or completely depleting previously deposited plasma charge. The underlying mechanisms that can be responsible for VUV-induced charge depletion are determined by exposing plasma-charged SiO2/Si samples to monochromatic-synchrotron radiation with photon energies in the range from 8 to 18 eV. Charge depletion was observed only for photon energies smaller than 13 eV. For photon energies between 8 and 11 eV, photoinjection of electrons from the Si into SiO2 conduction band is identified as the process responsible for charge depletion. For photon energies between 11-13 eV, field emission of electrons from Si into the oxide due to electric-field enhancement at the Si-SiO2 interface is believed to be the charge-depletion mechanism. Qualitative photoinjection and field-emission models convincingly explain all experimental measurements.

This work was supported by the National Science Foundation under grant No. DMR-0306582. The SRC is a national facility, funded by NSF under grant No. DMR-0084402.

9:00am **PS2-WeM4 The Characteristics of a Neutral Beam Angle using a Low Angle Reflected Neutral Beam Etching System**, ***D.H. Lee**, S.W. Hwang, J.S. Lee, S.H. Oh, Y.H. Lee, Y.-J. Kim, S.W. Choi, W.-S. Han*, Samsung Electronics Co. Ltd., S. Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage causing physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. The neutral beams recently investigated for the anisotropic etching are generated by a low angle charge exchange collision of an ion beam in the range from 50 to 500eV (hyperthermal ions) with a flat surface. The characteristics of the neutral beam formed after the charge exchange collision such as the neutralization efficiency, neutral beam energy and its distribution, scattering angle of the neutral beam, etc. are the important in the nanoscale device etching characteristics. When an energetic ion collides with the surface, various reactions of the incident ions with the surface are occurred. The collision of ions having a high energy or a high incident angle with the surface increases the possibility of sputtering or implantation, however, the collision of ions having a low energy or a low incident angle with the surface increases the possibility of reflection. The reaction phenomena between the surface and incident ions have been mostly studied with the incident ion energy range from keV to MeV for ion implantation or surface analysis, however, the reactions phenomena with the energy range less than 1 keV, which is important in the application of neutral beam etching, have not been investigated. Therefore, in this study, the variation of angle distributions of neutral beam after the low angle reflection of the low energy (<600eV) ion beam on the flat surface were investigated using double faraday-cup and the etch characteristics for the angle distribution changes were also investigated.

9:20am **PS2-WeM5 Quantitative Characterization of Ions and Si Surface Interactions - Estimation of Plasma-Induced Defect Generation Probability**, ***K. Eriguchi**, D. Hamada, M. Kamei, H. Fukumoto, K. Ono*, Kyoto University, Japan

The plasma damage induced by ion bombardment has become one of crucial issues from the viewpoints of the physical thickness in scaled devices. Quantitative analysis of the plasma-induced defects is requisite for understanding the mechanism and realizing high performance devices. In

this article, ions and Si surface interactions during plasma processing are quantitatively analyzed by novel techniques, providing the defect (charge trapping site) density and defect generation probabilities. Samples were exposed to two different plasma sources, DC and ECR with various biasing, gas mixtures and process time. N-type Si wafers with the low resistivity of 0.02 Ωcm were mounted on the stage and exposed to plasma sources. Combined with plasma diagnostics, two optical analyses, spectroscopic ellipsometry and photoreflectance (a modulation spectroscopy) were conducted to identify the damaged layer thickness with the 4-layer (air/layer-1/layer-2/Si substrate) model, the mechanical strain developing in the vicinity of the surface determined by the Si transition energy change, and the defect density (charge trapping site) by a novel method based on the surface potential change calculation. Also the surface layers were evaluated by a resistivity measurement. We have observed the characteristic structure change in the damaged layers with the relaxed mechanical strain (approximately 0.1 %) and the charge trap site generation with significant densities of $10^{12}$ $cm^{-2}$, along with plasma exposure time. Hence we have finally determined the defect generation probabilities per an impinging ion as $10^{-3}$ - $10^{-5}$ $s^{-1}$ in the present ion energy and plasma density ranges. The difference is attributed primarily to that in the measured bias voltage (-300 V for DC and -50 V for ECR) dominating the energy of ions accelerated in the sheath, although the ion energy distribution function has to be taken into account for further discussion. This ion energy effect is confirmed from the difference in damage-layer thickness by ellipsometry as well as from the etching simulation. The calculated defect densities in the damaged layer are considered to affect device performances in terms of the increase in power consumption by plasma-induced junction leakage. The obtained defect generation probability is a key parameter for understanding the mechanism of ions and Si surface reactions as well as plasma process designs.

9:40am **PS2-WeM6 Plasma-Catalytic Removal of Nitrogen Oxides**, ***M.M. Morgan***, *E.R. Fisher*, Colorado State University

Nitrogen oxides ($NO_x$), pollutants produced primarily from engine exhaust, contribute significantly to global air pollution. To reduce $NO_x$ emissions, catalysts involved in exhaust treatment must be improved. A greater understanding of fundamental chemical gas-phase and gas-surface processes is, therefore, required. One promising solution is plasma-catalytic processes for removal of pollutants, specifically nitric oxide (NO), from exhaust gases. Our imaging of radicals interacting with surfaces (IRIS) technique allows us to simultaneously examine the gas-phase, perform surface analyses, and probe the gas-surface interface. Here, we have used IRIS to address the fundamental issue of $NO_x$ removal by measuring relative gas-phase densities and by examining the steady-state surface reactivity of plasma-generated species on catalytic surfaces. Data from relative gas phase density studies suggest that increased water content and applied rf powers are required to diminish a majority of NO emissions. Preliminary IRIS data suggest that NO scatters off of surfaces with a high probability. Additional data on the internal temperature of NO in these systems as a function of plasma parameters will also be discussed.

10:40am **PS2-WeM9 New Insight into Fundamental Ion-Surface Interactions**, ***M.J. Gordon***, *X. Qin, K.P. Giapis*, California Institute of Technology **INVITED**

Collisions of ions with surfaces at low energy (<1 keV) are important in reactive ion etching of semiconductors, dielectrics, and metals. For example, ion bombardment can have a strong effect on etch rates, profile anisotropy, and selectivity through physical sputtering, momentum-assisted product removal, and modification of reaction rates. Fundamental understanding of these issues requires detailed information about the scattering processes which occur under different bombardment conditions. To this end, we have conducted scattering experiments involving mass-filtered ions ($F^+$, $CF_x^+$, $NF_x^+$) with tunable energy (50-1000 eV) and high flux (monolayers/s) on several surfaces (Si, Al, Ag) to look critically at collision kinematics, charge exchange processes, and surface reaction products. Topics to be discussed include: (1) electronic excitations in hard collision events (inelastic losses and $F^{++}$ formation); (2) pre-collision fragmentation of $CF_x^+$ ions which result in fast exit products such as $C^+$, $F^-$, and $CF^-$; (3) high yields of fast $F^-$; and (4) bimodal energy distributions of $F^+$ and $F^-$ species leaving Si and Ag surfaces. For instance, energy losses measured for single-scatter events of $F^+$ off Si and Al show that $F^{++}$ can be formed through a double electron promotion mechanism which "turns-on" above a critical collision energy. Velocity analysis of daughter fragments from $CF_3^+$ impact on Si and Ag point to several situations where fast exit species ($C^+$+$F^-$ and $F^+$+$CF^+$ with energies > binary collision predictions) are formed as a result of the projectile ion breaking apart before the hard collision step. Finally, energy analysis of $F^+$ and $F^-$ leaving Si and Ag surfaces shows two distinct scattering channels: one associated with a binary-like, single-scatter elastic event and another narrow, low-energy channel that cannot be explained as simple sputtering. These results illustrate that in many instances, product species can show significant inelastic losses as well as faster-than-SIMS behavior which may have a dramatic impact on profile evolution in plasma etching. In addition, energy analysis of both the positive and negative ion products associated with fluorinated ion scattering provides indispensable clues about the physics of reactive ion etching.

11:20am **PS2-WeM11 Investigating Fundamental Etch Limits: Molecular Dynamics Simulations of Sub-10 nm Feature Fabrication**, ***J.J. Végh***, *D.B. Graves*, University of California, Berkeley

As semiconductor devices are continually scaled down in size, individual device features are approaching the molecular scale. Fundamental knowledge of the mechanisms of the etch process at very small scales will be necessary to effectively design future etch-enabled pattern transfer schemes. Additionally, it is currently unclear how small features can be made using conventional processing methods. Molecular dynamics (MD) simulations have been carried out to examine the fundamental characteristics of etching very small features on silicon and diamond carbon surfaces. These features are created in simulation through bombardment of surfaces by idealized ion and radical beams (i.e. with perfectly controlled confinement, directionality, and energy). For very small beam diameters (less than 2 nm) a novel mode of hole formation is seen in MD in which the substrate atoms are displaced laterally by the ion beam, but not sputtered. This results in uniform holes with high aspect ratios and the formation of a densified, amorphized region laterally surrounding the hole. Lateral densification occurs from atoms that have been displaced from the hole void region during bombardment. As the beam diameter is increased to ~2 nm and beyond, sputtering is seen with yields comparable to those at steady state on bulk flat surfaces. The effects of redeposition on the side walls of the hole in relation to hole uniformity, achievable aspect ratios, and other feature characteristics are discussed. The effects of ion mass, quality of beam confinement, and the dynamics of ion-surface collisions are also addressed. The addition of chemistry to the inert ions (fluorine and fluorocarbon radicals and ions) is also discussed, and its effects on the hole formation processes are illustrated.

11:40am **PS2-WeM12 Fragmentation Dynamics of Energetic Fluorinated Ions on Inert and Reactive Surfaces**, ***X. Qin***, *M.J. Gordon, K.P. Giapis*, California Institute of Technology

Fluorinated ions with energies between 50-1000eV are important in plasma etching and deposition of materials used in the semiconductor industry. However, the scattering dynamics of molecular ions with surfaces are still not well understood in terms of fragmentation and energy transfer. We report results on the collision of mass-selected ions, such as $SF^+$ and $SiF^+$, with Si and Ag surfaces under UHV at impact energies relevant to plasma processing conditions (< 1 keV). Positive and negative products leaving the surface were analyzed in both mass and energy under high flux bombardment conditions (~monolayer/s) to compare with fragmentation of $CF_x^+$. Results show that daughter ions leaving a relatively inert surface (Ag) are much more energetic (not SIMS-like) than those from a reactive surface like Si. Characteristic overlaps in the velocity spectrum of species leaving the target surface suggest that a pre-dissociated projectile scatters nearly elastically off a target atom and breaks apart after the hard collision step. For instance, several daughter ions ($S^+$, $F^+$, $F^-$, $SF^+$) leave the surface at velocities much larger than expected for an elastic deflection of the molecular ion projectile. Product distributions (chemical identity and energy content) with respect to impact energy for a similar series of projectile ions (i.e., $SF_3^+$, $SiF_3^+$, $CF_3^+$) will be compared to understand the dynamics of how molecular ions fragment upon impact. Detailed reaction channels that lead to the formation of scattered products and etching of the surface will be discussed.

12:00pm **PS2-WeM13 Optical Second-Harmonic Generation to Study Plasma-Surface Interaction in Silicon Materials Processing**, ***J.J.H. Gielis****, *P.M. Gevers, P.J. van den Oever, A.A.E. Stevens, H.C.W. Beijerinck, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Surface and interface properties increasingly govern device performance in microelectronics, therefore, obtaining profound knowledge of these properties in real time during plasma processing is essential. In this respect, the nonlinear optical technique of second-harmonic generation (SHG) is very promising, as it has proven to be an ultra-sensitive probe for surface and interface states such as dangling bonds and strained Si-Si bonds in crystalline Si (c-Si) surface science.[1] In this work the real time and spectroscopic SHG response of amorphous silicon (a-Si) will be addressed in two areas of plasma processing, ion-assisted etching of c-Si and deposition of hydrogenated amorphous silicon (a-Si:H). In addition, spectroscopic ellipsometry was used to deduce linear optical properties. The

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experiments were carried out under well-defined conditions in high vacuum setups, using ion and radical beams to circumvent the complexity of the plasma.[2] Ion bombardment of c-Si using a low-energy $Ar^+$-ion gun (70-1000 eV) results in a layer of a-Si with a thickness of several nanometers. For fundamental photon energies from 1.35-1.75 eV, the SHG signal increases with an order of magnitude upon ion bombardment and it is shown that the SHG signal is governed by a two-photon resonance at 3.36 eV, related to modified Si-Si bonds at the a-Si/c-Si interface with an additional a-Si surface contribution. In the 0.8-1.1 eV fundamental photon energy range the increase in SHG signal is even stronger. It is discussed that the time-resolved SHG signal is governed by dangling bond creation and annihilation dynamics at the a-Si surface and a-Si/c-Si interface. Thin films of a-Si:H deposited on c-Si by a $SiH_3$ dominated beam have been investigated with SHG in the same photon energy ranges. For many applications, such as heterojunction solar cells, the abruptness of the a-Si:H/c-Si interface is crucial. Also in this system the SHG signal displays a strong resonance at ~3.3 eV from the a-Si:H/c-Si interface. It will be demonstrated that real time SHG provides a method to distinguish between direct heterointerface formation and nanometer-level epitaxial growth at a very early stage of film growth.

[1] U. Höfer, Appl. Phys. A 63, 533 (1996).
[2] J. W. Coburn and H. F. Winters, J. Appl. Phys. 50, 3189 (1979).

**Plasma Science and Technology**

**Room: 606 - Session PS1-WeA**

**Plasma-Wall Interactions**

**Moderator:** E.V. Barnat, Sandia National Laboratories

1:40pm **PS1-WeA1 Real-Time and Wafer-to-Wafer Control Strategies to Address Seasoning of Plasma Etching Reactors**[1], *A. Agarwal*, University of Illinois at Urbana-Champaign, ***M.J. Kushner***, Iowa State University

Seasoning of plasma etching reactors refers to the deposition of materials on the wafer and non-wafer surfaces of the chamber that change the fluxes of reactants to the wafer. This influence results from changes in reactive sticking coefficients of radicals and ions on surfaces that change the density of gas phase reactants, the removal of materials that add to the reactive fluxes to the wafer and changes in electrical properties. The negative consequences include drift, either during a process or wafer-to-wafer, in etch rates or uniformity of the process. In this paper, we discuss results from a computational investigation of the seasoning of reactors and, in particular, the use of real-time and wafer-to-wafer control strategies to eliminate process drift. These results were obtained using the Virtual Plasma Equipment Model, an implementation of sensors, actuators and control algorithms in the Hybrid Plasma Equipment Model.[2] The demonstration system is $Ar/Cl_2$ of Si in inductively coupled and capacitively coupled plasmas in which redeposition of etch products on walls and the wafer change reactive sticking coefficients and produce etch blocks. Sputtering of dielectrics in contact with the plasma introduce additional etch-block capable species. The diagnostics include etch rate sensors, optical emission and bias power. Actuators include power supply voltage, gas flow rate and gas mixture. We found that use of real-time-control to stabilize processes during a single etch and wafer-to-wafer control are sometimes complicated by the changing state of the wafer compared to the walls. For example, the wall conditions at the end of the prior wafer and beginning of the next wafer do not necessarily change however the new wafer does not have redeposition products. As such, actuators must be reset for the new wafer. Multiple sensors-and-actuators may be needed to account for the transition between neutral limited to ion limited processes as wall and wafer conditions change.

[1]Work supported by the Semiconductor Research Corporation and National Science Foundation.

[2] S. Rauf and M. J. Kushner, "Virtual Plasma Equipment Model: A Tool for Investigating Feedback Control in Plasma Processing Equipment", IEEE Trans. Semiconductor Manufact. 11, 486 (1998).

2:00pm **PS1-WeA2 Chamber Walls Coatings during Hard Mask Patterning of Ultra Low-k Materials: Consequences on Cleaning Strategies**, ***T. Chevolleau***, LTM, France, *M. Darnon*, LTM-CNRS, France, *T. David*, *N. Posseme*, CEA-LETI-MINATEC, France, *J. Torres*, STM, France, *O. Joubert*, LTM-CNRS, France

Changes in chamber wall conditions (e.g., chemical surface composition) are identified as one of the main causes of process drifts leading to changes in the process performance (etch rates, etch profiles, selectivity, uniformity …). The impact of a metal hard mask on the coating formed on the chamber walls during dielectric etching processes and reactor dry cleaning procedure has been investigated. We have used a technique based on x-ray photoelectron spectroscopy (XPS) to monitor the chemical composition of the layer deposited on an electrically floating sample placed on the top of a patterned wafer exposed to typical plasma processing conditions. By using this simple technique, the $Al_2O_3$ sample surface (or other chamber walls materials) is, similarly than the chamber walls, bombarded by low energy ions. Since the wafer is simultaneously bombarded by high energy ions, the gas phase is fed by etch products which get redeposited on the electrically floating $Al_2O_3$ sample and on the chamber walls surfaces. We have patterned porous SiOCH damascene structures using a TiN hard mask. After hard mask opening in a silicon etcher using $Cl_2$ based plasmas, we have shown that the chamber walls are coated by a thin SiOCl layer containing small concentrations of Ti. After photoresist removal in the same etcher (with an $O_2$ plasma), the chamber walls coating is oxidized leading to the formation of a mixed SiOx-TiOx deposit. The cleaning strategy to remove this coating from the chamber walls consists in using a two step cleaning procedure: (1) a $Cl_2$ based plasma (Ti removal) followed by (2) a $SF_6/O_2$ plasma (SiOCl species removal). During low-k etch in an oxide etcher using fluorocarbon based chemistries, the chamber walls are coated by a fluorocarbon layer containing a significant Ti concentration. We have developed a two step cleaning procedure: (1) a $SF_6$ plasma to remove the fluorocarbon layer and Ti based species and (2) an $O_2$ flash plasma (for a short time) to clean up the remaining carbon from the chamber walls.

2:20pm **PS1-WeA3 How Electron Density and Collision Rate Reflect the Properties of Chamber Wall and Substrate in IC Manufacturing**, ***M. Klick***, *L. Eichhorn*, Plasmetrex GmbH, Germany, *R. Benson*, *D. Steckert*, Micron Technologies, Inc.

Chemically active plasmas as every process plasma interact with the driven electrode and chamber wall. The wall and the electrode is heated and material as byproducts and material from the substrate condense preferably at the chamber wall. Without any additional influence, the parameters of the plasma reach an equilibrium, depending on the external parameters of the discharge as RF power. On the other hand the often used assumption that neutrals in a plasma have room temperature is quite questionable. Hence the indirect heating of the gas by the RF power was really underestimated despite this is one of the major reason of the so-called first wafer effect. There are two reason for the gas heating; the collision with fast ions in the boundary sheathes and the heating of chamber wall without proper 'thermal grounding' and a subsequent heating of the gas by the now hot surface of these chamber parts. Some authors have shown a significant increase of the gas temperature up to 1000 K in a RF plasma. The heat transmission resistances depends on the material, surface roughness, cleanliness and contact pressure. We will start at the experimental example of an increase of the surface temperature of the driven electrode at a 300 mm semiconductor production chamber with dual frequency excitation and the characterization of varying the torque of screws used for mounting. The temperature increase is characterized by the decrease of the electron collision rate. The collision rate, provided by the Self Excited Electron Resonance Spectroscopy, depends via the ohmic heating on the density of the neutrals and so finally on the gas temperature. Furthermore we will provide a qualitative discussion of the temperature effects, in particular resulting in a higher weight of stochastic heating mechanisms. The second example is the interaction of of an substrate, here a 300 mm wafer covered by mainly a polymer mask, an the plasma, in particular the electron collision rate. The interaction of plasma physical mechanisms as electron heating the plasma chemistry is analysed in the same way as indicated above.

2:40pm **PS1-WeA4 Surface Reactions of Atomic and Molecular Chlorine on Anodized Aluminum Surface in Chlorine Plasmas**, ***J. Guha****, *V.M. Donnelly*, University of Houston

Surface recombination reactions of Cl atoms on anodized aluminum have been investigated by the "spinning wall" technique in chlorine plasmas. Desorption of $Cl_2$ formed due to delayed (i.e. Langmuir-Hinshelwood) recombination of Cl atoms on the spinning surface was detected by mass spectrometry, and surface concentrations were measured in-situ by Auger electron spectrometry. Cl recombination probabilities were measured over a wide range of Cl atom flux by varying the plasma pressure and power. $Cl_2$ desorption was monitored over a time scale of 0.8 to 38 ms after the surface was exposed to the plasma (corresponding to the rotation frequencies of 35,000 and 800 rpm, respectively). The decay of $Cl_2$ desorption flux is highly non exponential within this time scale. Langmuir-Hinshelwood Cl recombination coefficients ($\gamma_{Cl}$) were measured by extrapolating the desorption flux to t = 0. For a typical condition of 5mTorr, 600W $Cl_2$ plasma the desorption flux was $2.8 \times 10^{15} cm^{-2} s^{-1}$ at t = 0. Absolute Cl atom densities close to the surface were measured by optical emission spectroscopy and Xe actinometry. $\gamma_{Cl}$ values ranged from 0.01 to 0.1 and were found to increase with increasing power and decrease with increasing total pressure. From the lowest pressure, highest power condition (1.25 mTorr, 600 W) to the highest pressure, lowest power case (20 mTorr, 100 W), the percent $Cl_2$ dissociation varied from 28% to 6%. With plasma off, $Cl_2$ also adsorbs on the surface, and desorbs over the same 0.8 - 38 ms time scale. Consequently $Cl_2$ adsorption competes with Cl adsorption with the plasma on, particularly at high pressure and low power. Physisorbed $Cl_2$ appears to block adsorption sites on the surface, thereby reducing the recombination probability, as observed. From Auger analysis of the surface during exposure to a 5mTorr, 600W $Cl_2$ plasma, the surface stoichiometry was found to be $Al_{3.2}Si_{3.3}O_{7.6}Cl$. Auger analysis of the surface at different plasma conditions suggests that less than 10% of adsorbed Cl atoms actually participates in surface recombination.

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3:00pm **PS1-WeA5 Impact of Cu Contamination on Chamber Walls on Via-Hole CD Shift in Cu Dual Damascene Etching**, ***H. Hayashi***, *K. Sato, K. Yamamoto, T. Kaminatsui, A. Kojima, I. Sakai, M. Hasegawa, T. Ohiwa*, Toshiba Corporation, Japan

With shrinkage of ULSI design rule, Cu wiring and low-k materials such as SiOC and poly arylene ether film (PAE) have been introduced to reduce RC delay in the metal interconnects. Furthermore, wafer-to-wafer repeatability of etching processes becomes a major concern. Therefore, controlling the chamber wall condition has been widely studied. In the SiOC etching process, fluorocarbon based plasma is used, which forms fluorocarbon film on the chamber walls. Typically, chamber cleaning is performed using oxygen based plasma, which removes the fluorocarbon film. Cu, which is sputtered from the Cu wiring exposed to the plasma during etching, deposits on the chamber walls and possibly remains, even after chamber cleaning. In this report, the influence of this Cu contamination on etch performance is studied. The stacked films of the PAE/SiOC hybrid dual damascene (DD) structure[1] for 45nm- node logic device were sequentially etched in the same chamber (all-in-one process). Wafers with Cu surface which becomes exposed during DD etching were etched, and it was found that the via-hole critical dimension (CD) of the second wafer of a lot decreased by 20 nm compared to the first wafer. However, $SiO_2$ and resist etch rates did not show any significant change. Then, plasma analyses using optical emission spectrometry with a high resolution of 0.1 nm were carried out to investigate the cause of the via-hole CD shift. It was found that the Cu emission intensity in the plasma of the second wafer was higher compared with the first wafer. This Cu emission intensity increase originated from the Cu deposited on the chamber walls during etching of the first wafer. Then, a wafer was etched after a chamber cleaning process to remove Cu was carried out, and it was found that the via-hole CD was the same as the first wafer. The Cu emission intensity became equivalent to that of the first wafer, also. The Cu emission intensity had a correlation with via-hole CD shift. Thus, Cu optical emission is sensitive to Cu contamination on the chamber walls, and the monitoring of Cu emission is an effective method of controlling the via-hole CD shift.

[1] A. Kajita et. al., Proc. of IITC (2003) p.9.

4:00pm **PS1-WeA8 Plasma-Wall Interactions in Inductively Coupled Plasma Reactor and a Novel Method for Wall Condition Control**, ***H. Singh***, Lam Research Corporation **INVITED**

Semiconductor technology has been aggressively scaled from micron sized features to 45 nm features over the last three decades . For the upcoming 32 nm technology node, total variation from all sources for a typical gate etch process is expected to be less than 2 nm. In addition, many new materials are being introduced in recent etch stacks, adding to the productivity challenges due to increased likelihood on non-volatile etch by-products on chamber walls. Plasma-wall interactions have significant impact on the chemistry of low pressure (<100 mTorr) plasmas. Therefore, control of chamber wall condition is crucial for achieving the desired process capability. Waferless Auto Cleans (WAC) have been demonstrated as essential in controlling wafer to wafer process repeatability in volume manufacturing above 65nm node. WAC removes etch by-products deposited during the wafer etch, minimizing drifts in chamber condition. However, ensuring no buildup of etch by-products on reactor walls is not sufficient to meet the productivity requirements of sub-65 nm node in many cases. Advanced Chamber Condition Control technology (AC3$^{TM}$) is a novel method to significantly enhance the productivity of etch systems in volume production. AC3 involves deposition of a thin film on the reactor walls prior to wafer processing, thereby eliminating drift in the wall condition during production. Impact of changes in the wall conditions due to chamber wet cleans, parts aging and variability are significantly reduced, allowing CD control at the nanometer level.

4:40pm **PS1-WeA10 Recombination of Oxygen Atoms on Dynamic Stainless Steel Surfaces**, ***L. Stafford***, *J. Guha, V.M. Donnelly*, University of Houston

We investigated the desorption of $O_2$ molecules from electropolished stainless steel surfaces following Langmuir-Hinshelwood (L-H) (i.e. delayed) heterogeneous recombination of oxygen atoms, using the spinning-wall technique. In this experimental set-up, a cylindrical section of the wall of an inductively coupled plasma reactor is rotated and the surface is periodically exposed to the plasma, a mass spectrometer, and an Auger electron spectrometer in separate differentially pumped chambers. Measurements can be performed over a wide range of O flux by varying the absorbed power (50-600 W) and total gas pressure before plasma ignition (1.25-20 mTorr). When the substrate is spun with the plasma on, a large increase in the mass spectrometry signals and Auger chamber pressure is observed with increasing rotation frequency. This increase results from O atoms that adsorb on the stainless steel surface when it is in the plasma and then recombine over the ~1-15 ms period probed by changing the rotation frequency. L-H recombination probabilities of O atoms were determined by extrapolating the $O_2$ signals to t = 0 (i.e. infinite rotation frequency). For example, at an O atom flux of $10^{17}$ $cm^{-2}s^{-1}$ obtained at 5 mTorr pressure and 600 W plasma source power, we have found a recombination probability of 0.035. This value is lower than those previously reported for O on stainless steel (e.g. 0.07 by Mozetic and Zalar, Appl. Surf. Sci. 158, 263 (2000), and 0.14 by Kiehlbauch and Graves, J. Vac. Sci. Technol. A 21, 660 (2003)). It is, however, similar to those previously obtained for O on anodized aluminum under comparable plasma conditions, where a Si-oxide layer was observed to form on the surface, due to the slow erosion of the quartz discharge tube. In the present study, analysis by Auger electron spectrometry during the recombination measurement also showed that the stainless steel surface became rapidly coated with a Si-oxide layer (Fe:Si:O atomic concentration ratios of ~1:2:5). This suggests that the recombination kinetics of oxygen atoms in this plasma reactor is determined by the coating on the walls, and not as much by the wall materials.

5:00pm **PS1-WeA11 The Effect of Wall Conditions on the Self-Limiting Deposition of Metal Oxides by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, *M.T. Seman, S.F. Szymanski,* ***C.A. Wolden***, Colorado School of Mines

Pulsed plasma-enhanced chemical vapor deposition (PECVD) has been engineered to deliver self-limiting growth (i.e. 1 Å/pulse) of metal oxides such as $Ta_2O_5$ and $Al_2O_3$. Pulsed PECVD may serve as a bridge between conventional ALD and PECVD, retaining monolayer control but with potentially much higher throughput. In this process the reactor walls are alternately exposed to atomic oxygen and metal precursors. The degree of adsorption in the latter step can dramatically influence both deposition rates and film quality. The impact of precursor adsorption on the plasma and gas-phase composition in these systems was measured using optical emission spectroscopy and quadrupole mass spectrometry, respectively. It is shown that the time scale for adsorption is much greater than gas-phase residence times. Adsorbed compounds significantly alter the reactor composition, particularly at the initiation of each pulse. As a consequence careful attention must be paid to reactor design and operation in order to control deposition rates and maintain quality.

## Plasma Science and Technology

## Room: 607 - Session PS2-WeA

## Plasmas and Polymers

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

1:40pm **PS2-WeA1 Activation of Polymer Surfaces by Electron Beam Generated Plasmas**, ***E.H. Lock***, *S.G. Walton, R.F. Fernsler*, Naval Research Laboratory

The activation of polymer surfaces via plasma exposure is one of the most powerful techniques to enhance the bond strength between the polymer surface and molecules, cells and thin films. Even though there are many established plasma techniques for the modification of polymer surfaces, there remain many unresolved questions regarding the most effective use of plasma processing because of the complexity of plasma-surface interactions. In order to guarantee quality and reproducibility of a given plasma process, numerous plasma effects and process parameters need to be taken into account. To ensure the maximum bond strength between a polymer and another material, the chemical and physical changes at the surface need to be well understood. Unfortunately, the conventional plasma sources are limited in their ability to address these problems and the lack of process control leads to problems with efficiency, scalability and material surface damage. Due to its unique characteristics, the electron beam generated plasma system developed at the Naval Research Laboratory allows access to operating conditions not available with traditional plasma methods. This plasma source provides individual control over the plasma parameters including plasma density, ionization region, electron temperature, ion and radical fluxes. Perhaps, the most important advantage of the system is that it minimizes the ion-induced damage to the substrate due to the inherently low plasma potentials. The objective of this work is to study the activation of polystyrene, polyethylene and polypropylene thin film surfaces exposed to plasmas produced in argon and SF6. Argon is inert and should limit surface modification to physical changes through bond breaking. SF6 provides a source of reactive radicals that can directly modify the surface. In both cases a wide range of process parameters was investigated, including pressure, gas flow rate, plasma exposure time, and substrate biasing (to increase ion energy). Ex-situ surface analysis included X-ray photoelectron spectroscopy, atomic force microscopy and various

wetting tests are applied to characterize the chemical and physical properties of plasma modified polymer surface.

2:00pm **PS2-WeA2 Impact of Plasma Etching Processes on 193 nm Photoresists: Etch Resistance and Line Width Roughness**, ***E. Pargon***, *J. Thiault, M. Martin*, CNRS, France, *J. Foucher*, CEA-LETI, France, *G. Cunge, O. Joubert*, CNRS, France, *Th. Lill*, Applied Materials Inc. **INVITED**

Successful pattern transfer by lithography and plasma etching requires minimal mask erosion, degradation and roughening. However, going to 193 nm based lithography in manufacturing several years ago brought new issues such as poor etching resistance of the photoresist masks during front end and back end processes. Indeed, the transition from 248 nm to 193 nm exposure sources has introduced significant changes in the composition of the photoresist (PR), including the removal of all aromatic functional groups due to their excessive absorption at 193 nm. Due to these important chemical changes, 193 nm PR not only exhibit poor etch resistance but are also thinner limiting strongly the 193 resist budget. Moreover, it was observed that 193 nm PR present severe surface roughening after plasma etching that can lead to wiggling and striations, impacting directly the resist Line Width Roughness (LWR). The critical issue is that PR degradation during plasma etching processes is possibly transferred into the underlayers, resulting in a polysilicon gate LWR above the requirements of the ITRS (1.4nm at 3σ for the 45 nm technological node). So far there is no real understanding on how different manufacturing operations may impact the resist roughness and its transfer into complex stacks of materials. In this work patterned and blanket 193 nm PR have been exposed to typical plasma etching processes involved in gate stack etching. In this work, we will show first correlations between etch rates (measured by ellipsometry), chemical analyses of the resist surfaces after plasma exposure (FTIR, XPS) and physical modifications on blanket resist substrates (using DSC and AFM), in order to better understand the etching and roughening mechanisms of typical 193 nm resists. The evolution of the patterned resist LWR and its transfer into the underlayer during the subsequent lithography and plasma etching steps are investigated by CD-AFM. We demonstrate that the resist LWR measured before etching is a key parameter in the final polysilicon LWR. Different plasma treatments applied to the 193nm photoresist patterns prior to all the following plasma etching steps can reinforce the 193 nm resist etch resistance and smooth the resist sidewalls thus reducing the LWR of the polysilicon gate. Our results also show that resist faceting induced by the ion bombardment plays a key role in the smoothening or roughening of the resist and pattern sidewalls.

2:40pm **PS2-WeA4 Plasma Etching Performance of Thin Polymeric and Photoresist Films**, ***N. Vourdas***, *G. Kokkoris, E. Gogolides*, Institute of Microelectronics, NCSR "Demokritos", Greece

In most cases of plasma processing of polymers, plasma etch rate (ER) is treated as being a constant value throughout the plasma process. However some studies have demonstrated that ER is actually a function of film thickness,[1,2] process time[3] or both. Similar observations have been recorded for the dissolution (development) rate (DR) of polymers, revealing a DR variation vs. film thickness. In this work we present plasma ER measurements via in situ spectroscopic ellipsometry (SE) of atactic (a-), isotactic (iso-) and syndiotactic (syndio-) poly(methyl methacrylate)-(PMMA) and poly(styrene)-(PS) films on Si and SiO2 under high density O2 plasma discharges, and observe variations of ER vs. time and thickness. Based on these findings along with data obtained from the literature we try to identify the reasons for these variations and deduce the key mechanisms controlling the plasma etching performance of thin and ultra thin polymeric films. Three kinds of ER variations are recorded: (a) ER increase (~8%) within the first stages of etching (~first 10 sec), followed by a gradual increase of ~20% until ~120 nm remaining film, (b) ~25% ER decrease after ~120 nm remaining film, and finally (c) ER drastic decrease at the final stages of etching (completion of etching) until ER=0. Variations (a) and (b) occur regardless the initial thickness, while the variation (c) strongly depends on process time, correlates with the surface roughness amplitude, and indicates means to control surface roughness of polymers (maximum surface roughness in this point). For ultra thin polymer films (less than ~100 nm) ER increase (region a) is not recorded; we attribute this to thin-film effects. These variations result in a decreased average ER of ultra-thin films compared to the ER of the thicker ones. These results are of interest both when ultra-thin polymers are used e.g. EUV lithography, chemical nano-patterning etc, or when high surface roughness is needed, e.g. antireflective coatings, super-hydrophobic coating fabrication etc.

[1]M. Tatoulian, O. Bouloussa, F. Moriere, F. Arefi-Khonsari et al, Langmuir 2004 20 p.10481
[2]N. Vourdas, A.G. Boudouvis, E. Gogolides, Microelectron. Eng. 2005 78-79 p.474
[3]X. Hua, S. Engelmann, G.S. Oehrlein et al, JVST B 2006 24 p.1850
[4]P. Paniez, M. Pons, O. Joubert, Microelectron. Eng. 1990 11 p.469.

3:00pm **PS2-WeA5 Fabrication of Organic Polymers with Tuned Properties and Their Correlation to Plasma-diagnostic Parameters**, ***G. Franz***, University of Applied Sciences, Germany, *D. Voss*, Plasma-Parylene Coating Services

Poly-parylene is one of the rare organic polymers which have passed the FDA criteria as long-term compatible for the human body. Films of the derivates C and N have been deposited applying cvd and pecvd (microwave). By a combined application of plasma diagnostics and surface analysis, is is possible to tailor the properties of the polymer poly-parylene over a wide range. In the border region, the plasma density rapidly falls with growing distance from the wall due to the strong shielding at microwave frequencies. In contrast to the usual expectation, the plasma density decreases with growing pressure for both ambients, argon and parylene. The electron temperature exhibits the expected hyperbolic behavior vs. pressure. Nevertheless, the higher deposition rate is the most significant proof of the higher density of polymer-building species as compared to cvd. As first consequence, in a pulsed plasma the ratio of the time constants of diffusion can be modeled applying the simplest approach proposed by Brown. For same power input, the plasma density in parylene is lower by more than one order of magnitude compared with argon, which is due to numerous other tracks of molecule excitation and electron loss. At the upper energy end, parylene-C definitely behaves as an electropositive gas, main loss of electrons caused by diffusion, whereas at low or medium energies, pressure-independent electron attachment is supposed to become the dominating loss mechanism leading to significantly lower plasma densities as compared to argon. Infrared spectroscopy shows the conservation of the ring structure during the plasma treatment. The contact angle exhibits a relatively flat response with respect to discharge pressure for cvd, stronger dependence for pecvd. The surfaces of the cvd-films are classically hydrophobic and lipophilic. This behavior is less pronounced in the pecvd-films. Films copolymerized with $CF_4$ are both hydrophobic and lipophobic in character and show very high roll-off angles (super-hydrophobicity). Subsequent plasma treatment with $Ar/O_2$ significantly reduces the contact angle against water (down to $30^o$). The dielectric constant has found to be very low with only a slight increase to low frequencies with nearly the same value at optical frequencies. Compared with previous works, the range for influencing these surface properties has been farther opened.

4:00pm **PS2-WeA8 Study of Plasma-Surface Interactions of Styrene and Vinylpyridine Polymers in $Ar/C_4F_8/N_2$ Discharges**, ***R.L. Bruce***, *T. Kwon, S. Engelmann, F. Weilnboeck, M. Sumiya, R. Phaneuf, G.S. Oehrlein*, University of Maryland, College Park, *B. Long, G. Willson*, University of California, Berkeley, *A. Alizadeh*, GE Electrics Global Research Center

$Ar/C_4F_8/N_2$ gas mixtures are being used for plasma etching low-k dielectric films. It is not fully understood how addition of $N_2$ affects the polymer surface of an organic masking material in a fluorocarbon-rich plasma environment. Therefore, the effects of $N_2$ addition in fluorocarbon plasma on polymers containing nitrogen (polyvinylpyridine) and without nitrogen (polystyrene) were investigated. The polymer surface after plasma exposure was analyzed using a number of characterization tools: ellipsometry (etch resistance), atomic force microscopy (AFM) (surface roughness), and x-ray photoelectron spectroscopy (XPS) (chemical composition). Through ellipsometric analysis, we found that the etch resistance was dependent on the steady state fluorocarbon (FC) layer created during plasma etching. With AFM, we have shown that the surface roughness decreased with $\%N_2$. Using XPS, it was found that while the fluorine content in the polymer surface continually decreased with increasing $\%N_2$, the nitrogen content increased until reaching a saturation level. Furthermore, significant differences in etch resistance, surface roughness, and chemical composition were found between polystyrene and polyvinylpyridine. We investigated whether the nitrogen in the polymer enhances the effect of the nitrogen in the plasma during exposure. In addition, we examined the relationship between the reduction of FC film thickness in remote plasma conditions and the enhanced etch rate of polymers in direct plasma conditions.

4:20pm **PS2-WeA9 Advanced Plasma Treatments for Cleaning and Protection of Metal Artefacts**, ***A. Milella***, University of Bari, Italy, *F. Palumbo*, CNR-IMIP, Bari, Italy, *S. Grassini, E. Angelini*, Polytechnic of Turin, Italy, *R. d'Agostino, F. Fracassi*, University of Bari, Italy

In the framework of conservation of cultural heritage, protection of metal artefacts from corrosion and degradation phenomena which take place during burial and /or during storage and exhibition, is of outstanding importance. Restoration procedures must be non-destructive, reversible, they have to respect the integrity of the objects and to satisfy specific requirements for preserving their aesthetic appearance. In this contribution we present the development of a non-destructive and reversible procedure for cleaning and protecting precious archaeological objects, mainly Ag-based alloys, in low pressure plasma. Reference Ag alloy with micro-

chemical and micro-structural features similar to ancient artefacts were used for the plasma treatments. To mimic the real artefacts, the specimens have been buried in the archaeological site of Tharros (Sardina, Italy) for 6 months. To accelerate the corrosion degradation 5% of NaCl has been added to the soil, since chlorides play a key role in the degradation of silver alloys during burial. Furthermore, to better mimic the patina present on real ancient artefacts (mainly consisting of AgCl and $Ag_2S$), the Ag-based alloys were also immersed in a solution of $Na_2S$. Cleaning of the tarnished specimens was carried out in RF hydrogen plasma. As detected by XRD and EDS analyses, the treatment effectively decreases the thickness of the patina to an extent which depends on the plasma treatment time. The hydrogen plasma removes the chlorides by forming HCl and this is accompanied by the reduction of oxidized silver ($Ag^+$) to metal silver ($Ag^0$). The conversion to $Ag^0$ can represent an advantage of the plasma cleaning with respect to conventional methods, generally leading to removal of silver from the artefact. Furthermore it is important to mention another benefit: existing cleaning methods are based on chemicals with environmental concerns. For protection of the Ag-based alloy from tarnishing, $SiO_2$-like coatings were deposited from a RF plasma fed with tetraetoxysilane/oxygen/argon mixture and the protective effectiveness was tested by electrochemical Impedance Spectroscopy (EIS) analyses. Results show that serious tarnishing of the coated samples only occurs after 72 h of immersion in 0.1 M $Na_2S$ solution. Chemical (FTIR, XPS) and morphological (AFM, SEM) characterization of the films will be also presented.

4:40pm **PS2-WeA10 Cell Growth on Plasma Deposited Micro- and Nano Patterned Teflon-Like Coatings**, ***P. Favia***, *E. Sardella, F. Intranuovo,* University of Bari, Italy, *P. Rossini,* Plasma Solution Srl, Spin off of the University of Bari, Italy, *R. Gristina,* Institute of Inorganic Methodologies and Plasma (IMIP) CNR, Italy, *M. Nardulli*, University of Bari, Italy

Plasma processes are widely used for biomedical applications.[1] Surface chemistry and morphology of substrates to be used in cell-adhesion and growth experiments can be modified by means of plasma (RF 13.56 MHz) PE-CVD from fluorocarbon feeds. Smooth and nano/micro-structured coatings could be obtained by tuning plasma parameters. Discharges fed with hexafluoropropylene oxide (HFPO) were run in continuous mode, and teflon-like coatings with different roughness values have been obtained by changing the afterglow distance with respect to the gas inlet of the plasma reactor.[2] In our previous work,[3] a study of nano-structured surfaces obtained from $C_2F_4$ was related to the deposition time. FT-IR, XPS, WCA, AFM and SEM analysis were used to analyze the chemical composition and the morphology of deposited coatings that were obtained by varying the substrate position in the plasma reactor. Nano-structured and flat coatings deposited on PET substrates were coated with a very thin homogeneous plasma deposited teflon-like film from $C_2F_4$ (6 sccm $C_2F_4$, 200 mtorr, 100 W, 21 s) to obtain surfaces with different roughness but identical chemical composition, to be used in cell-growth experiments. FT-IR, XPS and AFM data show that the "teflon character" (amount of the $CF_2$/C1s component) of the coating increases with the afterglow distance, as well as the hydrophobic character and the roughness ($R_{RMS}$ from 1± 0.2 nm to 350±43 nm). AFM images show different coating structures (e.g. nanopitted and cauliflower-like) as a function of the afterglow distance. Two coatings deposited at different positions, thus characterized by different morphology/roughness, have been selected for cell-growth experiments with 3T3 fibroblasts. Cell culture tests showed a different behavior when cell adhesion and growth were compared between nano-structured and flat coatings with the same surface chemistry. Acknowledgements: The MIUR-FIRB RBNE01458S project is gratefully acknowledged for the financial support.

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5:00pm **PS2-WeA11 Studies of Plasma Surface Activation for Adhesion Enhancement of Polymer Materials in Nanotransfer Printing**, ***D.Y. Lee***, *G.S. Oehrlein, D.R. Hines,* University of Maryland College Park, *C.M. Stafford, C.L. Soles, D.M. DeLongchamp, E.K. Lin*, National Institute of Standards and Technology

Recently, nanoimprint lithography (NIL) and nanotransfer printing (NTP) have attracted much attention because these techniques can be used to fabricate submicron structures at a lower cost and with higher throughput than conventional photo and electron-beam lithographies. For NTP involving thermoplastic polymer materials, a low processing temperature (below the glass transition temperature (Tg) of the polymers) is attractive to minimize distortion of printed layers and to control volume shrinkage of the polymers. One key factor influencing pattern transfer is the strength of adhesion between a printed polymer layer and a thermoplastic substrate. In this study, we systematically survey the factors controlling the adhesion between two polymer surfaces treated by plasma activation. Plasma treated poly(methyl methacrylate) (PMMA) films were transfer printed onto plasma treated polyethylene terephthalate (PET) substrates using NTP at 80 and 100 °C, 500 psi for 3 min. An inductively coupled plasma (ICP) process employing either O2 or N2 was used for surface activation of the polymers. In addition, we compared direct and remote plasma with gap structure to investigate the effect of ion bombardment on interfacial adhesion. With plasma activated samples, pattern transfer using NTP was possible at temperatures below the glass transition temperature (Tg) of both polymers. The enhancement of the polymer-polymer adhesion has been attributed to terminated functional group generated by the plasma surface activation and it mainly depends on the processing temperature and chemical composition of polymer and plasma chemistry. In-situ ellipsometry was used to measure changes in the refractive index and the thickness of the surface modified layer. Atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) measurements were performed on the plasma treated polymers immediately after treatment to minimize contamination effects due to atmospheric exposure. Surface energy and water contact angle of the modified films were also measured. Adhesion was evaluated both from a wedge test and from the NTP transfer efficiency, i.e., the aerial % of PMMA film successfully transferred to the PET substrate.

## Plasma Science and Technology

## Room: 606 - Session PS1-ThM

## Plasma-Surface Interactions II

**Moderator:** C.A. Wolden, Colorado School of Mines

8:00am **PS1-ThM1 Plasma Modification of Surface Traps in Mesoporous $TiO_2$**, ***D.J.V. Pulsipher***, *E.R. Fisher*, Colorado State University

Plasma surface modification can be effective in permanently modifying inorganic nanosurfaces. Particularly, mesoporous films formed from $TiO_2$ nanoparticles are interesting candidates for modification due to their important surface states needed for photovoltaic and photocatalytic applications. Plasma processing offers the opportunity of selectively modifying surface states to facilitate their investigation. Electron trap states in $TiO_2$-based devices, which are predominately located on $TiO_2$ particle surfaces,[1] can be detrimental in photovoltaic devices or beneficial in photocatalytic devices; consequently, controlling the quantity of these surface states by learning what causes and affects them will lead to more efficient devices. Here, low temperature inductively coupled plasmas are used to modify the surfaces of mesoporous $TiO_2$ films. Precursor gases such as $O_2$, $H_2O$, and $H_2$ have been used. Film surface states were primarily monitored by X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). The binding energy of a second O1s peak in the XPS spectra increases for increasing $O_2$ plasma powers in the range of 75-225 Watts, and the modified films have at least a 6% increase in surface altering oxygen sites which persisted for more than 6 months. PL results suggest[2] a decreased density of surface traps in oxygenated films.

[1] N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lagemaat,A. J. Frank, J Appl. Phys. Lett. 87, 202106.1 (2005).
[2] D. Zhang, J. A. Downing, F. J. Knorr, J. L. McHale, J. Phys. Chem. B 110, 21890 (2006).

8:20am **PS1-ThM2 A Robust Passivation-Enhanced Cryogenic Process used for Silicon Deep Etching**, ***L.E. Pichon***, *E.H. Oubensaid, C. Duluard, R. Dussart, P. Lefaucheux,* GREMI/CNRS, Université d'Orléans, France, *M. Boufnichel,* STMicroelectronics Tours, France, *P. Ranson,* GREMI/CNRS, Université d'Orléans, France, *L.J. Overzet*, University of Texas at Dallas

The need to scale down integrated circuits can be achieved by reducing transistor dimensions and also by 3D-integration. The latter takes advantage of high aspect ratio features and uses the silicon wafer volume as well as its surface. As a consequence, deep silicon etching is of crucial importance for 3D-integration. At GREMI laboratory, the cryogenic process is investigated for etching high aspect ratio structures in silicon. Generally, an inductively coupled $SF_6/O_2$ plasma is used to simultaneously etch silicon and deposit a passivation layer on the sidewalls at low temperature. When the wafer is warmed up to ambient temperature, the passivation film desorbs. Thus, the sidewalls are clean and have a low roughness.[1] The standard cryogenic process allows high etch rates but the passivation layer is not robust. This reduces the use of the cryogenic process in industry. To overcome this problem, passivation mechanisms have been investigated. A previous work has shown that $SiF_4$ plays a significant role in passivation layer formation.[2] Hence, it is possible to deposit a $SiO_xF_y$ passivation film in $SiF_4/O_2$ plasma when the silicon substrate is cooled down to cryogenic temperatures. Moreover, a study has shown that the robustness of the passivation film is enhanced when it is grown using a $SiF_4/O_2$ plasma rather than $SF_6/O_2$ plasma[2]. We will show the use $SiF_4/O_2$ plasmas to reinforce the passivation layer during a standard cryogenic process. In brief, the $SF_6/O_2$ anisotropic etching plasma is regularly stopped and the silicon substrate is exposed to a $SiF_4/O_2$ plasma to strengthen the $SiO_xF_y$ passivation film. This passivation-enhanced cryogenic process allows to significantly reduce the undercut (e.g. by a factor of 6 for a 10 µmm wide trench). Besides, the undercut can be completely eliminated for submicron trenches with an aspect ratio of 15 while the etch rate dropped only by a factor 1.3. We will present the passivation-enhanced cryogenic process and its performances.

[1] R. Dussart et al, J. Micromech. Microeng., 14 (2004) 190-196
[2] X. Mellhaoui et al, J. Appl. Phys., 98 (2005) 104901 .

8:40am **PS1-ThM3 3-D Profile Simulation of Silicon Etching: The Effects of Redeposition on Surface Roughening**, ***H. Kawai***, *W. Guo, Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

Line edge roughness (LER) on the sidewalls of gate electrodes in metal oxide semiconductor transistors is one of the most challenging issues in the microfabrication process today. Since the roughness does not scale with the feature size, the problem becomes more significant as critical dimensions get smaller for the future technology nodes. To understand LER, 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 in chlorine, hydrogen bromide and argon plasmas. We simulated the etching process using a dynamic Monte Carlo model, where the simulation domain is discretized into an array of cubic cells. The local surface conformation is fitted with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Our results show that the roughening in physical sputtering process is a strong function of ion incidence angle and redeposition of sputtered materials. At normal ion incidence, the surface remains smooth, but at very grazing ion incidence, the surface is roughened along the ion beam direction. At grazing angle, the roughness is enhanced by the redeposition of sputtered materials. The simulator is also capable of modeling the transfer of roughness from the photoresist layer to the underlying layer during the gate etching processes.

9:00am **PS1-ThM4 In Situ Measurement of the Ion Incidence Angle Dependence of the Ion-Enhanced Etching Yield in Plasma Reactors**, ***R.J. Belen***, *S. Gomez,* University of California Santa Barbara, *M. Kiehlbauch,* Lam Research Corporation, *E.S. Aydil*, University of Minnesota

In sputtering and ion-assisted etching processes, the material removal rate is quantified through the use of the sputtering yield, which depends on the energy and the incidence angle of the ions bombarding the surface. The sputtering or ion-assisted etching yield is defined as the number of surface atoms removed per ion impinging on the surface. The most widely used expression for the sputtering yield assumes that it is a product of separable functions of the ion energy and incidence angle and is proportional to the square root of the ion energy and f(φ), a function that attempts to capture the dependence of the yield on the ion incidence angle, φ, measured with respect to the surface normal. We demonstrate a technique to measure the dependence of the etching yield on the ion incidence angle by examining cross-sectional scanning electron micrographs (SEM) of features etched under realistic plasma conditions in an arbitrary plasma reactor. The idea for the technique described herein is based on the observation that ions bombarding the surface of a semi-circular shaped feature impinge on various points along the feature at different angles that span the range from normal incidence, , φ, = 0°, to grazing incidence, , φ, = 90°. Thus, the technique is based on measuring the etch rate as a function of position along the walls of features that initially have nearly semi-circular cross sections. These initial feature shapes can be easily obtained by wet or isotropic plasma etching of holes patterned through a mask. The etch rate as a function of distance along the feature profile provides the etching yield as a function of the ion incidence angle. The etch rates are measured by comparing digitized SEM cross-sections of the features before and after plasma etching in gas mixtures of interest. We have applied this technique to measure the ion incidence angle dependence of the Si etching yield in HBr, $Cl_2$, $SF_6$ and $NF_3$ plasmas and binary mixtures of $SF_6$ and $NF_3$ with $O_2$. Advantages and limitations of this method will be discussed.

9:20am **PS1-ThM5 Modeling of Angular Dependence in Plasma Etching Used for Profile Simulation**, ***W. Guo***, *Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

We have completely modeled the angular etching behavior for poly-silicon etching in chlorine chemistry as well as oxide in fluorocarbon chemistry at various operating conditions, including different neutral-to-ion flux ratios, ion energies and ion incidence angles. With this angular model incorporated into the 3-dimensional profile simulation, we can quantitatively predict the line-edge roughness on the sample sidewall. We developed the angular model within the framework of the translating mixed-layer kinetics model described previously. Unlike other kinetics models, we estimated the concentrations of chemical complexes based on the surface composition and assumptions of random atomic mixing and bonding within the top surface layer. Angular curves of various fundamental reactions including physical sputtering, ion-induced etching and dangling bond creation are analyzed using simulation tools such as TRIM. Based on those individual angular curves we predicted the apparent angular dependences at different neutral-to-ion flux ratios and ion energies for poly-silicon etching in chlorine plasmas as well as oxide etching in fluorocarbon chemistry. The simulated etching yields showed quantitative agreement with experimental data. At low neutral-to-ion flux ratio, the etching yield peaks around 60 degree off-normal angle then drops off, similar to physical sputtering. At high neutral-to-ion flux ratio, the etching yield monotonically decreases with ion incidence angle, which is indicative of ion-induced etching. Surface

fractions remain stable as a function of ion incidence angle for both poly-silicon and oxide etching, consistent with experimental observation.

9:40am **PS1-ThM6 Geometrical Effects on Etching Profile Evolution**, ***H. Fukumoto,*** *K. Eriguchi, K. Ono*, Kyoto University, Japan

Two-dimensional etching profile evolution in two different geometries, an axisymmetric hole and an infinitely long trench, has been calculated to clear the effects of geometrically different structures on etching profile evolution. In the simulation, $SiO_2$ etching by $CF_4$ plasmas is assumed because of widely employed processes for the fabrication of contact and via holes, which have various and unique geometrical shapes. The model takes into account the transport of particles in microstructures, together with surface reactions therein through sputtering, ion-assisted etching, chemical etching, and deposition. The model includes ions and neutrals ($CF_x^+$, $CF_x$, F; x=1~3) coming from the plasma, under different conditions of particle temperature, density, and ion energy. The simulation domain is enclosed by the sheath-surface interfaces and the feature surfaces of $SiO_2$ with an inert etching mask. The neutral particles from the plasma onto substrate surfaces are assumed to travel in microstructures with diffusive reflections on feature surfaces, while the ions accelerated through the sheath on the substrate travel with specular reflections on feature surfaces. The cell removal method is employed to represent the feature profile evolution, where the $SiO_2$ is represented by two-dimensional discrete cells. Numerical results indicate that the etching profiles of hole and trench have the similar tendency under different plasma conditions. However, the two etching profiles have some differences each other; the profile evolution is narrower and slower in the hole than in the trench, where the incident neutral fluxes are more reduced in the hole. Moreover, the profile of the trench has lateral etches such as undercut and bowing on sidewalls. The lateral etches decrease with increasing the ratio of neutral fluorocarbon fluxes, where the neutral fluorocarbons contribute to deposition. The velocity distribution of neutral particles also contribute to the difference of the etching profile evolution in the two structures; in effect, the velocity distributions are the more anisotropic in the hole, because more neutral particles interact with mask sidewalls in the hole, so that more anisotropic particles are conducted onto bottom surfaces after passing the mask features. Thus, it follows that geometrical structures contribute significantly to the behavior of neutral particles therein, and characterize the resulting etched profiles.

10:00am **PS1-ThM7 Growth Precursor Measurements and Study of Plasma Chemistry by Means of Mass Spectrometry**, ***J. Benedikt,*** *A. Consoli,* Ruhr-University Bochum, Germany, *M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands, *A. von Keudell*, Ruhr-University Bochum, Germany **INVITED**

The knowledge of absolute fluxes of reactive species such as radicals or energetic ions to the surface is crucial in understanding the growth or etching of thin films. These species have due to their high reactivity very low densities and their detection is therefore a challenging task. Mass spectrometry (MS) is an ultra sensitive technique and it will be demonstrated in this talk that it is an optimal choice for identification of growth precursors and for the study of plasma chemistry in general. MS measures the plasma composition directly at the surface, it is not limited by (non)existence of accessible optical transitions, as is for example laser spectroscopy, and when properly designed and carefully calibrated, it provides absolute densities of measured species. Two examples of application of MS will be presented. First, the composition of remote argon/acetylene expanding thermal plasma at the position of the substrate has been analyzed by means of molecular beam threshold ionization MS. More than twenty species have been detected including radicals with densities as low as $10^{10}$ $cm^{-3}$. Resonantly stabilized radicals, with $C_3$ being the most important one, have been identified as growth precursors of hard hydrogenated amorphous carbon films and the plasma chemistry pathway leading to their formation has been understood. In the second example, a temporal evolution of neutral species densities during initial stage of dust particle formation in a low pressure acetylene discharge has been measured. Mass spectra with time resolution of 100 ms have been obtained using a step-scan approach and they have been decomposed and quantitatively and qualitatively analyzed using Bayes statistics and calibration measurements. Based on a comparison of our results with in literature available positive and negative ion mass spectra measurements and plasma chemistry modeling of comparable plasma, the electron attachment to larger $C_nH_2$ species is proposed as an initial step in dust particle formation. Additionally, the analyses indicates the involvement of vinylidene, isomer of acetylene, or vinylidene anion in formation of first aromatic ring and it shows that surface reactions are a significant source of aromatic compounds.

10:40am **PS1-ThM9 Ground and Metastable Atom Densities in Rare-Gas Diluted $O_2$ and $N_2$ Plasmas and Silicon Oxynitride Growth**, ***T. Kitajima,*** *T. Nakano,* National Defense Academy of Japan, *T. Makabe*, Keio University, Japan

The application of rare gas diluted $O_2$ plasmas for oxide growth have gained interests due to the improved growth rate and film property. Metastable O atoms produced by rare gas metastables may contribute to the enhanced diffusion or reaction of the oxygen atoms at the interface of the film and the substrate. We have shown the increase of the metastable $O(^1D)$ atoms produced in the rare gas diluted $O_2$ plasma by VUV absorption spectroscopy.[1] The kinetics of the increased $O(^1D)$ atoms and the film growth can be explained by the deduced atom flux using diffusion model. In the study, we extend the scheme to the nitridation of silicon and finally to the oxynitride growth. The ground state $N(^4S)$ density in the rare gas diluted $N_2$ CCP is measured by the VUV absorption spectroscopy using 120 nm emission from the discharge light source ( $N(^4P) \rightarrow N(^4S)$ ). $N(^4S)$ density is $8 \times 10^{10}$ $cm^{-3}$ for 0.5 Torr and 30 W in pure $N_2$ CCP and stays $5 \times 10^{10}$ $cm^{-3}$ even for 1 % of $N_2$ fraction in Ar diluted $N_2$ plasma. The trend is also found for the case of He diluted $N_2$ plasma and should be due to the reduced energy loss of electrons by vibrational excitation. The grown nitrides are examined by the depth profiles of XPS and the growth rate corresponds to the trend of $N(^4S)$ density. Detailed results and the case of oxynitrides are shown in the presentation.

[1]T.Kitajima, T.Nakano, and T.Makabe, Appl. Phys. Lett. 88, 091501 (2006).

## Plasma Science and Technology

## Room: 607 - Session PS2-ThM

## Plasma Diagnostics I

**Moderator:** V.M. Donnelly, University of Houston

8:00am **PS2-ThM1 Ion Flux Measurements in an $Ar/NH_3/SiH_4$ - Remote Plasma using a Pulse Shaped Double-Side Capacitive Probe**, ***M.C. Petcu,*** *A.C. Bronneberg, M.A. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

In this work the investigation of an Ar - fed remote expanding thermal plasma (ETP) where $NH_3/SiH_4$ mixtures are injected downstream, is reported. Our interest is mainly focused on ion flux and ion densities measurements at different gas phase compositions. The ion and electron densities measurements using various methods and different plasma conditions have been previously reported in literature. For example, double and single cylindrical Langmuir probes have been successfully used to measure the ion density in non - depositing $Ar/NH_3$ ETP. A limitation of Langmuir probe measurements is to determine the ion densities in depositing plasmas, e.g. $Ar/NH_3/SiH_4$ mixtures, due to the formation of a resistive layer on the probe. An alternative approach is to use a single-side electrostatic probe, as already proposed in literature. This technique is compatible with the presence of insulating layers, showing the potential for absolute ion flux determination. The method is based on the discharging of an RF-biased capacitance in series with the probe. An alternative method, based on the use of pulse shaped double-side capacitive probe to measure ion flux in $Ar/NH_3$ and $Ar/NH_3/SiH_4$ plasma mixtures is here proposed. Our approach allows an accurate ion flux determination from the linear discharging of the capacitor connected in series with the collecting surface. Such approach could be easily implemented in a sensor for ion flux control in various discharges, e.g, in the case of a biased substrate to induce ion bombardment during film growth. When $Ar/NH_3$ mixtures are investigated, a decrease of the ion flux from $10^{18}$ to $10^{16}$ $cm^{-2}s^{-1}$ as a function of the $NH_3$ flow rate is measured and attributed to the consumption of Ar ions due to the charge exchange reaction between Ar ions and $NH_3$ molecules, followed by the dissociative recombination with low energy electrons. These results are also confirmed by Langmuir probe measurements. Furthermore, the addition of $SiH_4$ is showing an interesting behavior, i.e., a local increasing of the ion flux presently attributed to the formation of lighter ions, in conditions of high Ar ion depletion due to the high molecular gas flow rates. These measurements, together with mass spectrometry analysis, will be presented and commented in terms of plasma chemistry channels developed in an $Ar/NH_3/SiH_4$ plasma.

8:20am **PS2-ThM2 In Situ Plasma Analysis and Sheath Modeling of Silicon Deep Trench Etching in Capacitively Coupled Dual Frequency HBr/NF3 Plasmas**, ***M. Reinicke***, Dresden University of Technology, Germany, *S. Wege, S. Barth, A. Steinbach*, Qimonda Dresden, Germany, *G. Wenig, A. Kersch*, Qimonda Munich, Germany, *J.W. Bartha*, Dresden University of Technology, Germany

Facing critical dimensions below 50nm requires significantly improved knowledge about complex process mechanisms for DRAM technology development. To extend the knowledge of physical and chemical interactions during high aspect ratio (HAR) silicon etching using HBr/NF3/O2 plasmas, in situ plasma analysis has been performed at the latest generation of multi frequency capacitively coupled MERIE plasma reactors. Focus of this presentation is a detailed investigation of ion angular and energy distribution functions (IAEDFs) since these distributions are considered to be most essential for characterization of plasma-induced silicon deep trench etching using reactive plasma chemistries. Ion distribution functions (IDFs) were measured for basic Ar, HBr, NF3, as well as complex HBr/NF3/O2 plasma chemistries at the ground electrode of the plasma reactor using an in situ Hiden Analytical EQP500 combined energy and mass analyzer. Measured IDFs are compared to calculations using the Hybrid Plasma Sheath Model (HPSM) simulator. Difficulties in measuring IDFs are minimized by simulation of ion trajectories and a careful determination of the relevant transmission functions specific for the plasma monitor used. The hybrid-fluid simulator was additionally modified by implementation of differential cross sections resulting from ab-initio calculations for relevant ion-atom collisions. Finally, combination of measurement and simulation for investigation of the complex nature of multi frequency high voltage rf plasma boundary sheaths is shown to yield valuable information on the IAEDF for ions impacting the substrate and hence influencing etch process results.

8:40am **PS2-ThM3 Noninvasive Monitoring of Ion Current and Ion Energy during Plasma Processing**, ***M.A. Sobolewski***, National Institute of Standards and Technology **INVITED**

The bombardment of substrate surfaces by energetic ions plays an important role in plasma etching and other plasma processing applications. To obtain optimal results, ion current and ion kinetic energy must be carefully controlled. Unfortunately, directly measuring ion current or energy in situ, at a wafer surface during plasma processing, is difficult or impossible. To solve this problem, a technique for indirectly monitoring ion current and energy has been developed. It relies on measurements of the waveforms of rf current and voltage applied to the wafer electrode, which are interpreted by fundamental physical models of the plasma and its sheaths. The technique is noninvasive, i.e., there is no need to insert any probe into the plasma reactor, and it is suitable for use during actual processing in industrial equipment. This talk will describe the technique, the models it uses, and validation tests performed in an rf-biased, inductively coupled plasma reactor. It will also present results from experiments that demonstate the use of the technique to monitor ion current and ion energy during fluorocarbon etch processes and argon sputtering processes, including processes that were perturbed by reactor drift and equipment "faults." I will also discuss the present limitations of the technique and potential extensions of the technique to make it applicable to other plasma processes and other types of plasma reactors.

9:20am **PS2-ThM5 Application of an RF Biased Langmuir Probe to Etch Reactor Chamber Matching, Fault Detection and Process Control**, ***D.L. Keil***, *J.-P. Booth, N. Benjamin, C. Thorgrimsson*, Lam Research Corporation, *M. Brooks*, San Jose State University / Lam Research Co., *G. Curley*, Ecole Polytechnique / Lam Research Co., *L. Albarede, D. Cooperberg*, Lam Research Corporation

As feature size shrinks below 45 nm the demand for precision plasma etch process monitoring has increased. The final etched profile is determined by physical processes occurring at the wafer-plasma interface which are typically driven by neutral flux, ion flux and ion energy. However, typically only the RF delivery, gas flow, and chamber temperature are monitored. These measurements are too far removed from the actual physical processes of interest to be of value in tool matching, fault detection and advanced process control. This work examines the usefulness of an RF -biased planar Langmuir probe approach.[1] This method delivers precise real-time (10 Hz) measurements of the ion flux and tail weighted electron temperature and is insensitive to contamination and deposition on the probe. Data was taken during wafer processing, and indicates the utility of this approach for tool matching, process diagnosis, tool fault detection and advanced process control.

[1] J.P. Booth, N. St. J. Braithwaite, A. Goodyear, and P. Barroy, Rev. Sci. Inst., Vol. 71, No 7, July 2000, pgs. 2722-2727.

9:40am **PS2-ThM6 A New Diagnostic Method of Very High-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. To ensure this condition, 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 plasmas, produced by a variety of frequencies of 2 MHz to 60 MHz, and these plasmas are both the capacitively coupled and inductively coupled. 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 at the frequency of 60 MHz, 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 at the frequencies below 27 MHz 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 change in the electron energy distribution found in ICP was very systematic with the frequency, the gas pressures and the distances from the antenna. Thus the present method is quite innovative in that it is applicable to the potential fluctuating RF plasma and measurements are all done in a floating condition of probe.

10:00am **PS2-ThM7 On-wafer Real Time Monitoring of Charge-Build-up Voltages during Plasma Etching in Production Equipment**, ***J. Hashimoto***, *Y. Yatagai, T. Tatsumi, S. Kawada, M. Konishi, I. Kurachi*, Miyagi Oki Electric Co.,Ltd., Japan, *Y. Ishikawa, S. Samukawa*, Tohoku University, Japan

For requirements of high performance and large scale integration to semiconductor devices, transistor size has been shrunk down to nano-scale regime. Recently, 32nm gate length has been already developed and even 22nm gate length is under studying. As a result, gate insulator thickness of MOSFETs must be thin as less than 1nm in 22nm technology. Consequently, gate oxide breakdown caused by the plasma damage is a significant concern. In addition, extraordinary shape of via hole and etching stop caused by the electron shading effect must be solved to realize high aspect ratio via holes.These issues are attributed to charge-up during plasma etching processes. It is absolutely necessary for solution of them to monitor charge-up phenomena precisely. There are two typical methods to monitor them so far. One is measurement of electrical charge on the blank wafer after processing. The other is charge monitoring by using NVM(Nonvolatile memory). However, both methods dose not function for monitoring them in real time or on the actual patterned wafer. Consequently, the charge-up phenomena during device fabrication plasma etching can not be understood in detail.We succeed to monitor real time charge-up phenomena on the actual patterned wafer by using On-Wafer Monitoring Sensor newly proposed by Dr. Samukawa. In this study, an etcher for production was employed. From data of charge-up quantity under various etching conditions such as gas chemistry, RF power and pressure with various types of On-Wafer Monitoring Sensors, the charge-up phenomena can be revealed and will be reported in the presentation.

10:20am **PS2-ThM8 In-Situ Wafer-Based Plasma Sensor Analysis in Inductively Coupled Plasmas**, ***M.J. Titus***, *D.B. Graves*, University of California, Berkeley

In-situ, wafer-based plasma sensors are currently being explored to attack plasma process control and process development challenges. One such commercially available sensor tool is the PlasmaTemp$^{TM}$ sensor wafer, developed by KLA-Tencor. PlasmaTemp$^{TM}$ includes an on-board electronics module, coupled with wireless communication, which allows data storage of 30 temperature sensors embedded onto the wafer at different radial positions. In the present work, we focus on molecular gas (e.g. $O_2$) inductively coupled plasmas (ICPs). Wafer heating mechanisms in molecular gas plasmas can involve effects in addition to those identified in atomic gas plasmas (i.e. ion bombardment and ion-electron recombination). These mechanisms include thermal conduction from the neutral gas, when bulk temperatures are in excess of ~1000K, and atom recombination on the

wafer surface. We report a combination of plasma diagnostics and modeling, sensor wafer modeling, and experimental measurements for a variety of conditions in an $Ar/O_2$ inductively coupled plasma for wafer temperature measurements as well as for other plasma characteristics such as plasma density, ion flux and optical emission intensity.

10:40am **PS2-ThM9 Plasma Process Development and Control with Real-Time Critical Process Parameter Detection at the Wafer Surface**, ***M.R. Tesauro***, *R. Koepe, T. Remus,* Qimonda Dresden GmbH & Co. OHG, Germany, *G.A. Roche, P. MacDonald*, KLA-Tencor

Improved semiconductor manufacturing equipment / process diagnostics and control are ever more critical as the push toward ever smaller microelectronics device geometries continues. This is especially true for the fabrication process of controlled destruction: plasma etch. Improved plasma etch process diagnostics can be advantageous for initial development of stable processes to enable fast and profitable manufacturing ramp-up as well as assuring well-matched process results from the multiple plasma processing chambers required for volume manufacturing. Traditionally the focus of diagnostics and control has been on monitoring process chamber inputs (e.g. RF Power, pressure, gas flows, etc.) and outputs (e.g. product critical dimensions, etch rates, particle tests, etc.). Sensors which monitor the average plasma environment (e.g. plasma emission monitoring, advanced RF sensors, etc.) have further improved equipment and process control. Improved technologies now make possible process variable measurement directly at the wafer surface by incorporating sensors into an autonomous data collection sensor wafer. We present the results of such a wireless sensor wafer containing an array of temperature sensors to address issues of process stability and chamber matching. We will show how the unique properties of the thermal â?ofingerprintâ? of the actual plasma process measured near the wafer surface can be used to detect and correct differences between chambers and control for shifts following critical hardware replacement. In addition an example of the potential for process instability detection by thermal fingerprint on the wafer during development instead of during product ramp-up will be presented, showing the advantages and increasing necessity for time-resolved critical process parameter detection at the wafer surface.

**Plasma Science and Technology**

**Room: 606 - Session PS1-ThA**

**Plasma Diagnostics II**

**Moderator:** C.B. Labelle, Advanced Micro Devices, Inc.

2:00pm **PS1-ThA1 Development of Atomic Radical Monitoring Probe for Spatial Distribution Measurements and its Application to Reactive Plasma Processes**, ***S. Takashima***, Nagoya University, Japan, *S. Takahashi, K. Yamakawa, S. Den,* Katagiri Engineering Co., Ltd., Japan, *H. Kano,* NU-EcoEngineering Co., Ltd., Japan, *M. Hori*, Nagoya University, Japan

Atomic radicals such as hydrogen(H), nitrogen(N), oxygen(O), and carbon(C) play important roles in the reactive plasma processes. In order to realize nano-scale etching processes and fabricate high functional nano-structure materials using the plasma processes, it is indispensable to clarify the mechanism of the etching or the deposition processes and control the process plasmas at the particle level. Moreover, it is necessary to develop the plasma processes based on not external parameters such as power, pressure, and gas mixture but the internal parameters such as radical densities, their energies, and so on. In our previous studies, we have developed the compact measurement system of the atomic radicals such as H, N, O, and C in the reactive process plasmas. The technique of the system is a vacuum ultraviolet absorption spectroscopy (VUVAS) using an atmospheric pressure microdishcarge hollow cathode lamp (MHCL). The MHCL was 9mm in diameter. So, the system for measuring the atomic radical densities can be easily handled. Using the system, we have carried out the measurements of the densities in various process plasmas and clarified the behaviors of the radicals. However, the two opposite ports are necessary to measure the densities using the system. Moreover, it is difficult to measure the spatial distribution of the atomic radical densities in reactive process plasmas. In this study, we have developed the monitoring probe for the atomic radical density measurements. The probe consisted of the MHCL, the optical part, the probe part, and the VUV monochromator. The size of the probe installed to the plasma was 2.7 mm in diameter. The necessary port for the measurements was only one. Moreover, we can measure the spatial distribution of atomic radical densities by moving the probe along the chamber radius. Using the probe, we carried out the spatial distribution of the H radical densities in the remote $H_2$ plasmas. The densities drastically decreased from $1.2 \times 10^{12}$ $cm^{-3}$ to $4.4 \times 10^{11}$ $cm^{-3}$ near the chamber wall at the pressure of 1.33 Pa, the RF power of 300 W. It was considered that the drastic decrease of the H atom density near the wall was due to the surface loss of the H radical on the chamber wall made of the stainless steel. The atomic radical monitoring probe was the ubiquitous measuring tool because using the probe, anyone can measure the atomic radical densities in any material process plasmas at any time.

2:20pm **PS1-ThA2 Measurement of Absolute Density of Argon Metastables by using Laser Adsorption Spectroscopy**, ***T. Ohba***, *T. Makabe*, KEIO University, Japan

Absolute density of Ar metastables($1s_{3,5}$) was measured in a two-frequency capacitively coupled plasma (2f-CCP) in pure Ar by using Laser Adsorption Spectroscopy (LAS) in order to investigate the spatial profile. The axial density distribution of metastables is experimentally characterized as a function of pressure (25 mTorr - 100 mTorr) and bias amplitude (100 V - 400 V). Axial density profile of Ar metastables shows a broad peak in front of the electrode driven at 100 MHz, and gradually decreases toward the opposite electrode biased at 500 kHz. With decreasing pressure, the density approaches to more defusive profile as expected. The typical density of $Ar(1s_5)$ is $10^{11}$ $cm^{-3}$, and the density ratio between $Ar(1s_5)$ and $Ar(1s_3)$ changes from 10 to 9.3, when we increase the pressure. Under the present external plasma condition, the bias amplitude has less influence on the axial magnitude and distribution of the metastables. It implies the complete functional separation between the driving and bias power in the 2f-CCP in the present system. The spatiotemporal transport of low energy electrons will be discussed through the fundamental collision process of $Ar(1s_5)$ by using optical emission and absorption spectroscopy.

2:40pm **PS1-ThA3 Gas Phase Studies of CH3OH Plasmas Using Optical Emission Spectroscopy**, ***K.J. Trevino***, *E.R. Fisher*, Colorado State University

Plasmas are traditionally used for deposition, etching, and surface modification of various types of materials, most notably in the semiconductor industry. Plasma systems have recently been utilized in a non-traditional application, water remediation. Three steps are involved in this process; determining which organic molecules can be detected, developing effective detection systems, and establishing the efficacy of abatement. Recent studies of dense medium plasma systems have developed oxidation mechanisms for organic molecules, converted organic contaminants to less toxic species, and examined aromatic compound breakdown with GC/MS. Here, we have investigated the use of an inductively coupled plasma (ICP) system with optical emission spectroscopy (OES) for the purpose of non-intrusive detection as well as abatement of organic molecules in contaminated water. Our data demonstrate that not only is detection of organic molecule breakdown possible for a variety of species, but abatement is also possible. Currently we are able to detect <100 ppm contamination and are exploring this technique for the desired detection limits in the ppb range. OES data for the detection and abatement of CH3OH and larger organic molecules such as urea and methyl tert-butyl ether in aqueous solutions will be presented.

3:00pm **PS1-ThA4 Measurement of the Gas Temperature Distribution in UHF-ECR Dielectric Etching System**, ***H. Kobayashi***, *K. Yokogawa, K. Maeda, M. Izawa*, Hitachi, Ltd., Japan

Plasma etching is widely used for the fabrication of semiconductor devices. In this process, particle contamination continue to be an issue. Recently, for the purpose of controlling the particle transport, use of the thermophoretic force, that move the particles toward lower gas temperature region, has been investigated. We measured the particle behavior in plasmas by using UHF-ECR etching apparatus having a laser particle monitor. The laser particle monitor consist of 532nm-YAG laser, lenses to form the laser sheet light passing above the wafer, and CCD camera to detect the laser light scatted by particles. We injected particles into plasmas by gas puffing and we found that particles gathered above the wafer center, when plasma density was decreased at the wafer center. Though, particles moved away from the region above the wafer, when plasma density was increased at the wafer center. We simulated particle transport by considering gas viscous force and thermophoretic force. And, it was predicted that there existed gas temperature gradient of 1000 K/m. In this study, the gas temperature distribution across the wafer was investigated. The gas temperature can be assumed to be equal to the rotational temperature of the nitrogen molecules. Thus, we measured the emission spectra of the second positive system of nitrogen molecules. The rotational temperature was determined by comparison of the measured spectral profiles and theoretical spectral profiles calculated by assuming rotational temperatures. The emission from the plasmas was measured through the top plate. Nitrogen and $CHF_3$ gases were used for plasma discharge by considering the SiOC damascene etching. When plasma density was increased at the wafer center, the gas temperature at the wafer center and the wafer edge were 450 K and 460 K, respectively. On the contrary, when plasma density was decreased at the wafer center, the gas temperatures at the wafer center and the wafer edge were 410 K and 510 K, respectively. Consequently, we confirmed that the gas temperature distribution across the wafer can be controlled by changing plasma distribution and the gas temperature gradient of 1000 K/m can be made.

3:40pm **PS1-ThA6 Research at CPMI Towards Making EUVL a Success**, ***D.N. Ruzic***, *S.N. Srivastava, K.C. Thompson, H. Shin, J.R. Sporre, E.R. Ritz*, University of Illinois at Urbana-Champaign

Center for Plasma Material Interactions (CPMI) at the University of Illinois is currently expanding efforts to solve critical problems for timely implementation of extreme ultraviolet lithography. The research at CPMI is focused on variety of different problems being currently faced in this technology. A commercial extreme ultraviolet light source (XTS 13-35) is investigated to characterize the debris ejecta. A fully calibrated ion diagnostic device (spherical sector ion energy analyzer) is developed, which is used for measuring the ion debris fluxes and their energies in absolute units. Ion debris is measured both from Xe as well as Sn EUV sources. Several mitigation schemes are investigated and tested for their effectiveness in the XTS 13-35 source. Recent work towards debris mitigation includes gas curtain, pulsed foil trap, plasma based mitigation, mixed fuel experiments. In the case of mixed fuel experiments, by adding 5% of $H_2$ in the main fuel (Xe), the ion energies and fluxes could be reduced by half of the original value. Using pulsed foil trap mitigation, 4 keV $Xe^+$ ion flux could be reduced about 4 times whereas $Xe^{2+}$ ion flux were dramatically reduced by a factor of about 90. Mirror samples are exposed to the EUV source and erosion due to harsh plasma debris is measured for variety of different EUV compatible materials (C, MLM, Si, Mo, Pd, Mo-Au, Au). For example, the measured erosion on EUV exposed multilayer mirror (MLM) sample is about 13 nm ± 2 nm. Comparison with theory predicts the major damage from high energy ions itself, but also

indicates the role of neutral particles. To advance the debris diagnostic tool, the detector is further modified to account for neutral debris measurement. Ion and neutral debris measuring capabilities allowed us to perform life time testing. We have also studied the problems with Sn EUV sources and currently developing methods to clean Sn effectively from the mirror surface without actually harming the surface underneath. Reactive ion etching is found to be a viable solution and variety of different samples are tested and processed through the cleaning techniques. Encouraging results in this area has motivated us to do a full blown test in the EUV source and install an integrated cleaning system, which could run in a manufacturing environment.

4:00pm **PS1-ThA7 Inductively Coupled Plasma Radio Frequency Electrical Characteristic Measurement for Deposition of CNTs.**, ***W.-C. Chen***, Academia Sinica, Taiwan, *C. Mahony,* University of Ulster, UK, *K.-H. Chen,* Academia Sinica, Taiwan, *L.-C. Chen*, National Taiwan University

Here we investigate radio frequency (RF) inductively coupled plasma (ICP) as an in-line sensor for characterizing vertical aligned carbon nanotubes (CNTs) deposition plasma via correlation of the real/imaginary RF current/voltage. The plasma dual directional coupler (PDDC) was used to measure the forward and reflected voltage before the ICP matching network in Ar plasma. Then we introduce a homemade external circuit to give impedance Z, which includes the parasitic inductances of capacitors, parasitic capacitance of inductors and cable resistances. Component values in the circuit model can be determined by analysis of VHF (very high frequency) bridge and spectrum analyzer data. With arising reaction pressure in Ar plasma, the corresponding current & voltage will be change. The maximun current in Ar plasma can be observed at the pressure of 60 mtorr and power of 200 Watt. Indicating much higher electrons density and effective collision frequency in this plasma condition. Measured values of Z with rising RF input power of plasma shows the reactance X to vary from negative to positive values. These correspond with observed E to H transition in this ICP. We will discuss RF harmonics during CNTs deposition condition in Ar & CH4 and relate them to process repeatability and reliability.

4:20pm **PS1-ThA8 Process Control through Diagnostics and Understanding: Multi-frequency Discharges and Atmospheric Pressure Plasmas**, ***T. Gans***, Queen's University Belfast, UK **INVITED**

Despite its technological importance, power coupling and ionisation mechanisms in radio-frequency (rf) discharges are not yet fully understood. Of particular interest are multi-frequency discharges and recently developed non-equilibrium rf discharges at ambient pressure. Insight into the complex dynamics requires close combination of advanced diagnostics and specifically adapted simulations. Phase resolved optical emission spectroscopy (PROES) in combination with particle-in-cell (PIC) simulations reveal details on the dynamics within the rf cycle. Multi-frequency discharges can provide additional process control for technological applications. The electron dynamics exhibits a complex spatio-temporal structure. Excitation and ionisation, and, therefore, plasma sustainment is dominated through directed energetic electrons created through the dynamics of the plasma boundary sheath. These electrons are predominantly produced during contraction of the low frequency sheath. This can be understood in the following picture. During the phase of low-frequency sheath expansion power dissipation is highest which determines plasma heating. This power is, however, deposited into a large number of electrons in the vicinity of maximum sheath expansion. The dissipated power during the collapse of the low-frequency sheath is deposited into a much smaller number of electrons, since the electron density close to the electrode surface is significantly lower. The power dissipation per electron can, therefore, be higher during the sheath collapse, which then creates energetic directed electrons. Recently developed rf discharges at ambient pressure bear enormous potential for future technological applications providing high reaction rates without the need of expensive vacuum systems. Fundamental discharge mechanisms are, however, only rudimentarily understood. The atmospheric pressure plasma jet (APPJ) is a homogeneous non-equilibrium discharge. A specially designed rf μ-APPJ provides excellent optical diagnostic access to the discharge volume and the interface to the effluent region. This allows investigations of the discharge dynamics and energy transport mechanisms from the discharge to the effluent. PROES measurements in the discharge volume show similar excitation and ionisation mechanisms as in capacitively coupled rf discharges at low pressure. An interesting phenomenon is the interaction between the two plasma boundary sheaths.

## Plasma Science and Technology

## Room: 607 - Session PS2+BI-ThA

## Plasmas in Bioscience

**Moderator:** P. Favia, University of Bari, Italy

2:00pm **PS2+BI-ThA1 Time-of-Flight Secondary Ion Mass Spectrometry Analysis of Fibrinogen Adsorbed to Low-Fouling Tetraglyme Surfaces**, ***L. Mayorga***, *R. Michel, D.G. Castner, T.A. Horbett*, University of Washington

Antibody binding and ToF-SIMS were used to probe the conformation of fibrinogen (Fg) adsorbed to low and high fouling surfaces, including tetraglyme and FEP. Fg on implants plays a key role in the foreign body response (FBR) by mediating the adhesion of monocytes via the Mac-1 integrin.[1] PEO-like tetraglyme coatings generated via radio frequency glow discharge plasma display ultra-low Fg adsorption ($\Gamma_{Fg}$ < 10 ng/cm$^2$) from low concentration blood plasma solutions and low monocyte adhesion.[2] However, subcutaneously implanted tetraglyme still exhibits FBR encapsulation. With 3 mg/ml Fg in buffer (with tracer amounts of $^{125}$I-Fg added), $\Gamma_{Fg}$ increased to 60 ng/cm$^2$ on tetraglyme and 800 ng/cm$^2$ on FEP. Nonetheless, the actual amount of $\Gamma_{Fg}$ on glyme surfaces under any of the conditions tested is not enough to fully account for the observed monocyte adhesion in vitro. The Fg on glymes was relatively low, but adhesion was relatively high, suggesting that Fg might be in a more potent state on the glymes. To understand the role of Fg conformation in mediating monocyte adhesion, we used a monoclonal antibody to measure the degree of monocyte binding site (γ 377-395) exposure on adsorbed Fg. Epitope exposure per ng of adsorbed Fg was highest on low-fouling tetraglyme samples pre-adsorbed with low concentration Fg. In addition, ToF-SIMS was used as in previous studies[3] to characterize the conformation of Fg adsorbed to the tetraglymes. By pairing these two different approaches to study the conformation of adsorbed Fg, we will be able to relate surface analysis results with cell and protein binding data, which will allow us to better understand protein-cell interactions in the FBR.

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2:20pm **PS2+BI-ThA2 Interaction of Peptide Ions with Self-Assembled Monolayer Surfaces**, ***J. Laskin***, *O. Hadjar, P. Wang, Z. Yang*, Pacific Northwest National Laboratory

Interaction of ions with surfaces is an area of active research in surface science relevant to a broad range of other scientific disciplines such as materials science, mass spectrometry, imaging and spectroscopy. Our research is focused on fundamental understanding of interaction of hyperthermal (1-100 eV) peptide, protein and polymer ions with organic surfaces under ultrahigh vacuum conditions. Two major processes are dominant for this range of collision energies: reactive and non-reactive scattering of ions and ion loss on the surface as a result of neutralization or soft-landing (SL) of projectile ions. Scattering and deposition of large ions following collisions with SAM surfaces was studied using a unique Fourier transform ion cyclotron resonance mass spectrometer developed in our laboratory. Ion activation by collisions with surfaces is rather poorly characterized from a fundamentals perspective. We explored the effect of the physical and chemical properties of SAM surfaces on the energy transfer in collisions. Our studies demonstrated that energy distribution functions are well-represented by Maxwell-Boltzmann distributions indicating fast thermalization of ions by collisions. A notable discovery was a sharp transition between slow unimolecular decay of large ions at low collision energies and near-instantaneous decomposition (shattering) in higher energy surface collisions. Shattering of ions on surfaces opens up a variety of fragmentation pathways for large complex ions that are not accessible to conventional ion activation techniques. We have conducted first systematic study of several factors that affect SL of peptide ions on SAM surfaces. Deposition of peptide ions of different composition and charge state on SAM surfaces was followed by in situ and ex situ SIMS analysis. Peptide ions are attractive model systems that provide important insights on the behavior of soft landed proteins. We were able to measure for the first time the binding energy between peptide ions and hydrophobic SAM surfaces. We also demonstrated very strong binding of peptide ions to hydrophilic surfaces and covalent linking of peptides to reactive SAMs. Fundamental principles derived from such studies of interaction of protonated peptides with hydrophobic or hydrophilic surfaces are relevant

to the understanding of the transport of biomolecules through membranes in living organisms and provides a clear pathway for highly-selective preparation of biological surfaces.

2:40pm **PS2+BI-ThA3 A New Approach to Nano-Fabrication of Functional Structures : Wet Nanotechnology and Bio Nano Process**, ***I. Yamashita***, Matsuhita Electric Industrial Co. Ltd. Japan **INVITED**

We proposed a new method for the fabrication of functional nano-structures in an aqueous solution, which could be used in semiconductor processes or electron devices and can be called a wet nanotechnology (WNT). The WNT employs aqueous solutions as the environments for nano-blocks, which are thermally agitated, to self-organize into the functional nano-structures. The final structures could be designed in the initial nano-block structures and functional nanostructures can be produced economically. This is the same with the way how the lives are carrying out in the nature. So far, we invented several processes using the WNT and proteins, which collectively we named Bio Nano Process (BNP).[1] So far, the BNP produced several key components of the electron devices. Firstly, a floating nanodots gate memory (FNGM) was produced employing a cage-shaped protein, apoferritin (collaborative project with Dr. Fuyuki at NAIST). Nanoparticles (NP) were biomineralized in the apoferritin cavity, which produced homogenous NPs such as CdSe, ZnSe, CdS, Co3O4, InOx, Fe2O3 and so on. A 2D ordered array of the apoferritins with NP was made on the Si wafer by self-assembly and heat-treated The obtained 2D ordered array of NPs was applied for the FNGM.[3] Secondly, we used 7nm Fe2O3 NPs, which were produced and placed on Si wafer by the BNP, as the nanometric etching mask to fabricate Si single crystal nanocolumn (a collaborative project with Dr. Samukawa at Tohoku Univ). The neutral beam etching successfully produced single crystal Si columns with 7nm diameter and high aspect ratio4. We further extended the BNP application and produced a large bio-template for single electron transistor (SET).[5] A ball and spike type protein supramolecules which has a central cage-shaped protein and protruding spikes was produced by the self-assembly of genetically made chimera proteins. These experimental results demonstrated that the BNP can fabricate the inorganic nanostructure using protein supramolecules. The WNT and BNP are opening up a biological path to nano-electron devices.

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3:40pm **PS2+BI-ThA6 Improvement of the Adhesion of PECVD-deposited DLC Films on Metals**, ***J.-C. Schauer***, *J. Winter*, Ruhr-Universität Bochum, Germany

The coating of a material with a wear and corrosion resistant coating is required in many realms. Concerning biomedical applications for example a coating of implants made of shape memory alloys such as NiTi is needed to protect the implant against wear and corrosion and the surrounding tissue against the release of metal ions. One candidate for such a coating is a thin film of diamond like carbon (DLC, hard configuration of a-C:H), since it is very hard, wear resistant, has a low friction coefficient, is chemically inert and biocompatible. But up to the present the coating of most metals with a DLC film has shown many difficulties. The bad adhesion between substrate and DLC is due to the poor chemical binding between most metals and carbon and/or due to high internal stresses occurring in DLC films. One promising technique to overcome the problem of poor adhesion of the coating to the substrate is the deposition of a very thin interface layer on the substrate before the coating is deposited on top. By a correct material choice such an interface can replace weak coating-to-substrate bonds with strong coating-to-interface layer bonds and interface layer-to-substrate bonds. Another effect of the interface layer can be the reduction of internal stresses in the interface region. By the use of at least two layers on top of each other the probability of pinholes or defects going from the surface to the substrate is decreased. This is especially important if toxic substrates are to be coated. Therefore, we use a thin amorphous hydrogenated silicon (a-Si:H) film as an intermediate layer between metal and DLC film to enable the coating of metals with DLC films. Due to the formation of strong silicide bonds the adhesion of DLC films on metal is increased significantly. The thin films under investigation are deposited in a capacitively coupled discharge with acetylene and silane as precursor gases for the DLC and a-Si:H films, respectively. The a-Si:H films have a thickness of only several 10 nm, whereas the DLC films can have a thickness of 100 nm or more. It will be shown that an intermediate layer of a-Si:H significantly increases the adhesion of DLC on metals and how the film properties of a-Si:H and DLC influence the strength of adhesion. The influence of different parameters like applied power, substrate temperature, hydrogen content in the films, and others on the adhesion of the films also under durability tests will be presented.

4:00pm **PS2+BI-ThA7 Polymeric Surfaces Chemical Modification by Low-Pressure Plasma Processes for Application to DNA Array Technology**, ***P. Rivolo***, Politecnico di Torino, Italy, ***S. Lo Bartolo***, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, *D. Perrone*, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, *S. Fiorilli*, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, *I. Vallini*, LaTEMAR, Ctr of Excellence funded by MIUR; Biodiversity SpA, Italy, *C. Ricciardi*, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy, *M. Quaglio*, Lab. Materiali e Microsistemi, Italy; Politecnico di Torino, Italy, *G. Mantero*, Biodiversity SpA, Italy, ***C.F. Pirri***, LaTEMAR, Ctr of Excellence funded by MIUR; Politecnico di Torino, Italy

The low cost of production, the easy handling and the large variety of polymeric materials favour them as attractive candidates to replace classic glass slides in micro-array biomolecular diagnostics. However, the lack of reactive functional groups, at polymeric surfaces, makes difficult their use as substrates for immobilization of molecules such as DNA fragments, in either cDNA or oligodeoxyribonucleotide (ODN) format, for a variety of applications to DNA micro-array technology including microscale sequencing, mRNA expression monitoring and single nucleotide polymorphism analysis. In this contribution, modification of surface chemical properties of cyclo olefin copolymer (COC), polystyrene (PS), polyethylene (PE) and polycarbonate (PC) is reported. The surface of polymeric substrates, properly molded by hot embossing, was modified introducing monotype functional groups[1] and using them for subsequent covalent grafting of linker molecules, active for amino-oligonucleotide probes immobilization.[2] A first step consisting of non-equilibrium low-pressure air and water RF plasma was used to activate the polymer surface, forming oxidized species such as -C-O-, -C=O, -C-OH, -CHO, -COOH. Successively, a liquid-phase reduction by a $NaBH_4$ solution was carried out to increase the yield of –OH groups in order to enhance the amount of covalently grafted 3-aminoproylsilane (3-APTES), a reaction carried out by vapour-phase process.[3] The last step was performed by a liquid phase reaction between glutaraldehyde and amino-groups of grafted 3-APTES. After this, polymer surface shows -CHO species suitable for the reaction with the amino-modified probes. Characterization of the functionalised polymeric surfaces was performed by contact angle measurements and reflection-absorption infrared spectroscopy (RAIRS)[4]. Modification efficiency of different polymers substrates was evaluated by well-modified Arrayed Primer EXtension (APEX) protocol with colorimetric and fluorimetric detection methods.

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4:20pm **PS2+BI-ThA8 Patterning of Plasma Polymers for Bioarrays**, ***G. Mishra***, *S.L. McArthur*, University of Sheffield, UK

Modern day technological advancements have allowed us to overcome critical challenges posed in proteomic research. As a direct result of developments in miniaturisation and automation, the current market has seen ever growing numbers and varieties of high density arraying slides being used for proteome research and application. Needless to say that these developments have been matched with state of art instrumentation and data analysis packages to achieve true automated multiplex analysis. Yet, issues like non-specific adsorption of biomolecules to solid substrate and control over the orientation during immobilization need addressing. Key to these issues could be the precise control over surface modification and patterning. Plasma polymerisation presents a versatile approach to surface modification of these devices. The range of monomers available for plasma polymerisation makes this manufacturing approach even more suitable for use in systems where multiple coatings with specific properties are required for a single device. The ability to spatially define reactive regions to reduce non-specific background adsorption is integral to this project. 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. Plasma polymerisation when used in conjugation with photolithography has allowed us to simultaneously obtain high spatial and chemical resolution. Multivariate analysis of ToF-SIMS spectral and image data has allowed us to critically study and address issues associated with the chemical specificity and spatial resolution of the multilayer patterning approach. Our results suggest that complex multilayer plasma coatings can be produced without compromising the chemical properties of the deposited polymer layers.

4:40pm **PS2+BI-ThA9 BSA Adsorption onto Oxygen Plasma PTFE Modified Surfaces**, *B. Broze*, ***N. Vandencasteele***, Universite Libre de Bruxelles, Belgium, *P. Viville*, Materia Nova, Belgium, *R. Lazzaroni*, *M. Hecq*, Université Mons Hainaut - Materia Nova, Belgium, *D.G. Castner*, University of Washington, *F. Reniers*, Universite Libre de Bruxelles, Belgium

The adsorption of bovine serum albumine on surfaces is usually a first good test for potential biological applications. In this study, PTFE surfaces were exposed to a remote RF oxygen plasma. The plasma was characterized using optical emission spectrometry, whereas the PTFE surface was characterized using monochromatized XPS, dynamic contact angle and atomic force microscopy. The modified surfaces are then exposed to BSA. The presence of protein was then evidenced by the presence of the N1s peak in the XPS spectrum, by AFM images, and by the change in the contact angle. We show that at low plasma power (or DC-bias) and short treatment times, the contact angle decreases, leading to slightly more hydrophilic surfaces. Small amounts of oxygen (up to 5%) are detected on the surface. BSA adsorbs on these surfaces. An increase in the plasma power leads to an increase of the sample roughness and to an increase of the hydrophobicity. On superhydrophobic (angles above 160°) surfaces, BSA does not absorb any more. No oxygen is present in the XPS spectrum. A correlation was established between the change of the contact angle, the amount of adsorbed protein and the roughness. It is shown that the decrease of the contact angle, and the hysterisis between the advancing and receding angles are good probes for protein adsorption.

5:00pm **PS2+BI-ThA10 Composition and Structure Study of the AP Plasma Deposited Hydrophobic Thin Film**, ***C. Chen***, *W. Hsieh*, *C. Liu*, *W. Hsu*, *C. Lin*, Industrial Technology Research Institute, Taiwan

In this study hydrophobic thin films were prepared by plasma enhanced chemical vapor deposition at atmospheric pressure by means of two layer compositions on the surface of glass. The bottoms were using Ar and hexamethyldisilazane (HMDSN) as the carrier and monomer gases respectively to deposit silicon oxide and offer microstructure. The deposited glasses were further coating a hydrophobic layer using fluoroalkylsilane (FAS) as the chemical precursor. Meanwhile, to evaluate the effects of fluorine contained of the water repellency of substrate, CF4 was introducing into the plasma zone during plasma depositions. The chemical structure of the thin film was characterized using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopies (FTIR) measurement. Morphologies and topography of the coatings were examined by scanning micro spectroscopy (SEM) and atomic force microscopy (AFM). FTIR measurement indicated that a SiO2 layer can successful deposit on the glass and the porosity of the thin films was direct proportion with thin film thickness. The SEM results indicated that the thickness of the thin films increasing almost linearly with coating times and the thickness was about 143nm after three times of deposition. AFM results reveal nano-clusters were well distributed on the surface after two layers deposition but introducing CF4 during deposition will slightly reduced the roughness because of decompose reaction between CF4 plasma and the Si atom in the thin films. The deconvolution of the C1s core-level spectra and atomic ratio from XPS measurement indicate FAS can be react and deposited on the top layer. The contact angles of the double layers was 134.0 degree which are great than traditional fluoro-polymer such as polytetrafluoroethylene (PTFE). Otherwise, bypass introducing CF4 during plasma polymerization the contact angle will increased to 143.3 degree indicate the AP plasma can be used to deposit super hydrophobic thin film on the glass surface.

## Plasma Science and Technology

## Room: 4C - Session PS-ThP

## Plasma Science and Technology Poster Session

**PS-ThP1 An In-situ Diagnostic to Detect Charging during Plasma Etching**, ***E.R. Ritz***, *D.N. Ruzic, R. Ramasamy*, 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 titanium with alternating layers of $SiO_2$ and titanium. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The silicon dioxide layers act as insulators to create discrete measurement layers, provided by the titanium layers. The titanium 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 less than one micron thick, with vias ranging in diameter from 1 micron to only 20 nanometers, thereby producing aspect ratios of 1:1 to 30:1. Results from the diagnostic will be shown for various etching recipes.

**PS-ThP2 The Effect of Radio-Frequency Bias on Electron Density in an Inductively Coupled Plasma Reactor, Measured by a Wave Cutoff Probe**, *M.A. Sobolewski*, National Institute of Standards and Technology, ***J.H. Kim***, Korea Research Institute of Standards and Science

Inductively coupled plasma reactors allow greater, more independent control of ion energy and ion flux than is possible in traditional capacitively coupled plasma reactors. Nevertheless, even in inductively coupled reactors, it is unlikely that perfectly independent control can be achieved. The application of radio-frequency (rf) substrate bias, which is intended to only affect ion energies, may also produce changes in the plasma electron and ion densities and the total ion flux. Such changes are generally believed to be small, but it is not clear how small. Modeling studies of inductively coupled plasmas usually do not consider these bias effects. Experimental measurements of the effect of bias on electron density have been made, using Langmuir probes or microwave interferometry, but the data reported so far are quite limited and often appear to be contradictory. The accuracy of some results may be in doubt, since measured changes are comparable in size to systematic errors present in the measurement techniques. To provide a better characterization and understanding of the effect of bias power on electron density, we performed a detailed study in Ar, $CF_4$, and $Ar/CF_4$ plasmas. We measured the electron density with a wave cutoff probe, which avoids problems with deposition and rf compensation that may affect the accuracy of Langmuir probes. The effect of rf bias on electron density was measured as a function of source power, position, pressure, bias frequency, bias amplitude, and time. At selected experimental conditions, results from the cutoff probe were compared to Langmuir probe measurements, and both showed the same effects. Two types of bias-induced changes in electron density were observed. One was a gas composition effect caused by etch or sputter products liberated from the wafer surface. The other was an electron heating effect caused by absorption of bias power by plasma electrons. Simple models of each effect were derived and shown to yield quantitative predictions in agreement with the observations.

**PS-ThP3 Measurement of Ion Energy Distribution in Dual-Frequency Capacitively Coupled Plasma**, ***S.-H. Seo***, *H.-S. Lee, J.-B. Lee, H.-Y. Chang*, Korea Advanced Institute of Science and Technology

The ion energy distribution in a large-area and dual-frequency capacitively coupled plasma (CCP) was measured by using two methods, the noninvasive ion energy analyzer (NIEA) and the quadrupole mass spectrometer (QMS). The argon plasma was generated by 2 and 13.56 MHz RF powers, which were separately applied to two electrodes with a diameter of 600 mm and a gap distance of 50 mm between two electrodes. The NIEA detector was installed between the matching network and the electrode at two electrodes. It was found that the the energy distribution of ions incident to the low-frequency (LF) RF electrode exhibits a characteristic distribution with a series of peaks when 2 and 13.56 MHz RF power are applied simultaneously while it exhibits a single peak distribution or a well-known double peak distribution when a single RF power is applied or it is measured at high-frequency (HF) RF electrode. Those structured ion energy distributions were observed for a variety of the power ratio of two RF powers. The QMS equipment was installed inside the LF RF electrode. And, the energy distribution of ions incident to the LF RF electrode was measured by using the QMS and was compared with the ion energy distribution measured by the NIEA. The features of the ion energy distribution were analyzed and explained by the modulation of the sheath potential by two RF frequencies, which could be measured with the high-voltage probe at the electrode.

**PS-ThP4 Analysis of Plasma Electrical Characteristics during Arcing and the Development of Arcing Detector in rf Discharges**, ***K.Y.H. Kim***, KAIST, Republic of Korea

Arcing phenomena have become a fatal problem in TFT-LCD fabrication, semiconductor manufacturing, PECVD, and many other processes using plasma. But it has been unknown how arcing affects electrical characteristics of plasma. We investigated the sudden-electrical perturbation of plasma by arcing. The RF electrode was dc grounded to increase plasma potential and generate arcing. We measured floating potential, RF voltage and current to analysis the plasma-electrical variation by arcing. Experimental results show that the arcing in RF discharges change suddenly electrical characteristics of plasma and that especially amplitudes of both RF voltage and current decrease during arcing. And we described experimental results (plasma-electrical variation by arcing) analytically. Finally, using the arcing variation, we developed the equipment which can detect plasma arcing by non-perturbed method. This equipment was tested in real processing reactor like as semi-conductor etcher and showed the ability of sensitive arcing-detection.

**PS-ThP5 Diagnostic of Plasma Generated in Water by Time-Resolved Optical Spectroscopy**, ***C. Miron***, *M.A. Bratescu, T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

Electrical discharges in water are used for generation of ozone, oxygen, hydroxyl radicals and other chemically active species. These reactive species leads to favorable conditions for synthesis, as well as degradation of compounds. Therefore, electrical discharges have found applications in metal nanoparticles synthesis, water disinfection, biomedical applications. Numerous works have also presented concerning the electrical behavior of water subjected to high electric fields. Despite the progress, there is not yet a complete understanding of issues relating to the breakdown initiation process and the physics of charge creation in liquids. In this study, we investigate electrical and optical properties of a discharge process in water. Time resolved optical emission spectroscopy method is used to determine the reactive species generated in the aqueous system. An electrical discharge process in ultrapure water was generated between two cylindrical electrodes in a plastic vessel. Electrodes of different diameters and materials were used in the process. The electrical discharge conditions were varied in order to determine the evolution of reactive species generated in the water. The breakdown voltage and also the electrical current applied in the discharge were observed to be modified when using different materials of the electrodes and different interelectrode gaps, thus changing the plasma behavior. The water conductivity and pH values were also changed, depending on the electrode material used in the discharge process. The time emission spectra of hydrogen, oxygen atoms and hydroxyl radicals were studied in dependence with discharge voltage, pulse width, repetition frequency. A detailed analysis of different emission lines after the ignition of the high voltage pulse was realized, with modifying the voltage, pulse width, and repetition frequency.

**PS-ThP6 Diagnostics of a Microwave Plasma by Optical Computerized Tomography**, ***C. Tian***, *T. Nozawa, K. Ishibasi, M. Horigome*, Tokyo Electron LTD., Japan

A Radial Line Slot Antenna (RLSA) for surface-wave-plasma at 2.45GHz is a promising candidate with respect to increased process requirements for the large-diameter plasma. Diagnostics of such a kind of plasma was performed by Optical Emission Spectroscopy (OES) under various process conditions. Time-averaged computerized tomography has been developed to obtain a sliced 2D-image for optical emission from the RLSA plasma, which gives some useful information of spatial distribution of the relative net production rate of ions and radicals. The discharge chamber is about 35 cm in diameter and 20 cm in depth with a dielectric window 3 cm thick on the top. A smart optical scanner is amounted to the observe quartz window at the plasma diffusion level. The intensity of optical emission at selected wavelength throughout OES can be reconstructed to a spatial profile of species in RLSA plasma. We performed the measurement under low-k CVD process condition for the spatial distribution of species CFx. The

changes of spatial distribution of ions and radicals of CFx under different RF bias and stage temperature reveal some essential plasma dynamics relate to the property of Low-k film. It has been concluded that the optical computerized tomography provides a way for fast plasma diagnosis and efficient real time process control.

**PS-ThP7 Diagnostics in a Continuous Electron Beam-Generated Plasmas**, ***S.G. Walton***, *E.H. Lock, R.F. Fernsler*, Naval Research Laboratory

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 ($n_e > 10^{10}$ $cm^{-3}$) with low electron temperatures ($T_e < 1.0$ eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 5 eV) at surfaces located adjacent to the electron beam. Most systems under developed at NRL use a hollow cathode pulsed to high voltages to produce the electron beam, which of course, results in a modulated plasma. We have recently developed a continuous electron beam source and are investigating the plasmas produced using this source. In this work, we discuss the bulk plasma properties and the ion flux at electrodes located adjacent to the electron beam. A Langmuir probe is used to determine the plasma density and electron temperature, while an energy-resolving mass spectrometer is used to determine the ion energies and fluxes at electrodes. Together the diagnostics provide a comprehensive description of the system. These plasma parameters will be determined as a function of gas background, electron beam intensity, and electrode bias. This work was supported by the Office of Naval Research.

**PS-ThP8 In Situ Plasmas Diagnostics Study of a Commercial High Power Hollow Cathode Magnetron Deposition Tool**, ***C.H. Castano***, *D.N. Ruzic, B.C. Masters, M.J. Neumann, E.R. Ritz*, University of Illinois at Urbana-Champaign

A variety of plasma diagnostics can be used to study the detailed influence of parameter variation on the plasmas used for PVD and PECVD on a commercial 200mm iNOVA high power hollow cathode magnetron deposition tool. Because of the special plasma conditions, non-standard geometry, and some non-standard frequencies used, specifically designed diagnostics are preferable to commercial solutions. These diagnostics include Langmuir probe analysis for electron temperature and density, a Faraday cups to study ion energy and density, optical spectroscopy for ion species identification and energy, quartz crystal microbalances combined with electrostatic and magnetostatic filters for deposition rates and ionization fraction of the incident metal atom species. Initial results from the plasma studies will be shown and compared tto theoretical calculations for ionization fraction and efficiency.

**PS-ThP9 Application of Exhaust Line OES on Plasma-less Process for Advanced Process Control**, ***S. Han***, *Y.-J. Kim, S.W. Choi, W.-S. Han*, Samsung Electronics Co. Ltd, South Korea

Recently, APC(Advanced Process Control) using in_situ monitoring sensor become more important for the enhancement of production efficiency and quality control mainly FD(Fault Detection) in mass production to meet specs for reduced feature size. Moreover, it makes process development and ramp up of yield faster. So, many in_situ electrical and optical sensors are being evaluated to find more sensitive and appropriate sensor for each specific process or equipment in many chip makers. The requirements of external in_situ sensor should be low in the price to easily manipulate, small to install, and justly accurate in the detectability. Among them, exhaust line OES sensor holds limelight due to that it can be used for monitoring non plasma process as well as plasma process. In this study, it has been qualified that exhaust line OES is a best solution as a real time gas analyzer, which can monitor by_product generated from chemical reaction, which can optimize EPD (End Point Detection), pre_conditioning time like seasoning, and process drift like"first wafer effect" of many different processes. First of all, most important thing is to detect or monitor undesirable process excursion like air leak, which affects product yield.

Application of exhaust line OES on plasma_less process for Advanced Process Control Keywords: OES (Optical Emission Control), APC (Advanced Process Control), FD (Fault Detection).

**PS-ThP10 Dry Etching of Extreme Ultraviolet Lithography (EUVL) Mask Structures in Inductively Coupled Plasmas (ICP)**, ***D.Y. Kim***, *H.J. Lee, H.Y. Jung, N.-E. Lee*, Sungkyunkwan University, Korea, *T.G. Kim, B.H. Kim, J. Ahn, C.Y. Kim*, Hanyang University, Korea

Currently, extreme ultraviolet lithography (EUVL) is being investigated for next generation lithography. Among the core EUVL technologies, mask fabrication is also of great importance. In this work, we investigated etching properties of the EUVL mask materials such as $Al_2O_3$ (ARC : anti-reflected coating layer), TaN (absorber layer), Ru (buffer/capping layer) and Mo/Si multi-layer (reflective layer) in inductively coupled plasmas. Etch rate and etch selectivity of the mask materials were investigated by varying the gas flow, DC self-bias voltage ($V_{dc}$) and top electrode power. Based on the etch results of each layer, etching of stacked mask structures were carried out. The $Al_2O_3$ ARC layer could be etched with the etch selectivity close to 0.5 over the TaN absorber layer. The ARC/TaN stack could be etched with a high etch selectivity over the Ru buffer/capping layer.

**PS-ThP11 Multi-Level Resist Employing Physical-Vapor Deposited Amorphous Carbon**, ***H.T. Kim***, *B.S. Kwon, N.-E. Lee, H.J. Cho, B.Y. Hong*, Sungkyunkwan University, Korea

In this study, we investigated the fabrication process of multi-level resist (MLR) based on thin physical-vapor deposited (PVD) amorphous carbon (α-C) layer. Due to difficulty of patterning PVD α-C with a very high plasma resistance, etching characteristics of PVD α-C layer with the $SiO_2$ hard-mask were investigated in a DFS-CCP (dual-frequency superimposed capacitively coupled plasma) etcher by varying the process parameters such as different high-frequency/low-frequency combination ($f_{HF}/f_{LF}$), HF/LF power ratio ($P_{HF}/P_{LF}$), $O_2$ and $N_2$ flow rates in $O_2/N_2/Ar$ plasmas. The results indicated an increased etch rate of PVD α-C for the higher $f_{HF}/f_{LF}$ combination and for the increased low-frequency power ($P_{LF}$). And the etch rate of PVD α-C was initially increased and then decreased with increasing the $N_2$ flow rate in $O_2/N_2/Ar$ plasmas. Application of PVD α-C layer as a mask for etching of the TEOS-oxide in the stack of ArF PR/BARC/$SiO_2$/PVD α-C/TEOS-oxide/Si indicated a possibility of using a very thin PVD α-C layer as a mask layer in the MLR structure.

**PS-ThP12 Plasma and Electrical Characteristics of an Internal Linear Inductively Coupled Plasma Source for Flat Panel Display Processing**, ***J.K. Park***, *J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Inductively coupled plasmas (ICP) have been investigated for the processing of semiconductors and flat panel display devices as one of the high density ($10^{11} \sim 10^{12}$ $cm^{-3}$) and low gas pressure plasma sources. Especially, ICP was the most attractive among the high density plasma sources due to the advantages of simple physics and a simple source structure requiring no external magnetic field. In fact, as the plasma sources for the dry etching, even though capacitively coupled plasma (CCP) sources are currently utilized for the etching of thin film transistor-liquid crystal display (TFT-LCD) devices, to improve the throughput of the TFT-LCD device processing, high density plasma sources are preferred compared to the conventional CCP sources due to their higher processing speed. In this work, an internal-type antenna (double-comb type antenna) was used as an inductively coupled plasma (ICP) source for an extremely large area (2,300 mm x 2,000 mm) processing and its plasma and electrical characteristics were investigated using a Langmuir probe and an impedance probe, respectively. Also, the etch characteristics of the photoresist (PR), such as the etch rates and etch uniformities on the large area substrate by oxygen plasma were investigated. The results showed a strong dependence of the plasma characteristics such as plasma density and uniformity on the antenna arrangement, and, for an optimized condition, the PR etch uniformity less than 13% could be obtained within the substrate area.

**PS-ThP13 Characterization of a High-Temperature Flowing Oxygen Plasma Afterglow**, ***N.D. Vora***, Vanderbilt University, *D.A. Pejakovic, J. Marschall*, SRI International, *B.R. Rogers*, Vanderbilt University

In the last decade there has been a renewed interest in developing ultra high temperature ceramic composites (UHTCs) as potential construction materials for parts of sharp leading edge hypersonic space vehicles. Oxygen atoms are known to play an important role in this application environment. Oxidation properties of UHTCs have been traditionally studied either in thermal furnaces which provide negligible dissociation of oxygen molecules or in arc-jet tests which dissociates all of them. To attain partially dissociated oxygen environments at low pressures and high temperatures which are better representative of the application environment, we are using a flow reactor downstream to a microwave discharge. To quantify the effect of oxygen atoms on the oxidation mechanism it is necessary to characterize the flow and oxygen plasma afterglow chemistry that the sample is exposed to during oxidation. This work discusses computational and experimental characterization of the reactor over a range of process conditions. There is a lot of uncertainty in the kinetic data available in the literature for high temperature oxygen plasma afterglow chemistry. Sensitivity analysis of the reaction chemistry will be carried out to determine the dominant reaction in the plasma afterglow at relevant pressure and temperature conditions. The output from this model, specifically the oxygen atom concentration reaching the sample, will serve as an input for the subsequent modeling of the oxidation mechanism in the materials oxidized using this set-up. Thus this characterization effort will help in better understanding the high temperature oxygen plasma afterglow chemistry and also the quantitative effect of atomic oxygen on the oxidation properties of various materials.

**PS-ThP14 Performance Characteristics of Inductively Coupled rf Ion Source for Low-energy Neutral Beam**, ***M. Park***, KAIST, South Korea

Low-energy neutral beam sources are very promising candidates for the next-generation nano-processing. To realize high-flux low-energy neutral beam, we have developed a novel 13.56 MHz radio frequency inductively coupled ion source. Argon ion beam velocity distributions were measured by dye laser-induced fluorescence technique and compared with electrostatic retarding field analyzer(RFA). We describe the extraction system which enables our ion beam source to have high ion beam current densities at very low energy (<50 eV) region without broadening of beam divergence or energy in comparison with conventional ion beams. Synchronized Pulse biasing technique is applied when operating $SF_6$ pulsed plasma.

**PS-ThP15 Residue-free High Dose Ion-Implanted Resist Removal using a High Power $O_2/N_2$ Plasma Jet**, *M. Bhargava,* University of Houston, *A.K. Srivastava,* Axcelis Technologies, *W. Donner,* ***J.C. Wolfe***, University of Houston

The complete, damage-free and efficient removal of high dose ion-implanted (HDI) photoresist is one of the most challenging issues in integrated circuit manufacturing. The problem arises because a crust of implanted metal ions and vitrified carbon forms on the resist surface that is much less reactive to plasma ashing chemistries than unimplanted resist. The throughput limitation implied by this intrinsically low ash rate is compounded by the need to limit the wafer temperature to avoid popping, the explosive ejection of macroscopic crust particles due to thermally induced volatilization of the unimplanted resist layer beneath the crust. This paper describes the application of a high power $O_2/N_2$ plasma system to ashing of HDI photoresist. Reactant gas (typically $O_2$:$N_2$=9:1) is activated by a 2.5 kW, 2.45 GHz surface wave discharge in an air cooled quartz process tube 6 mm in diameter. The directional flow (3slm) of process gas at 80 Torr pressure produces a plasma jet that emerges from the end of the discharge tube and impinges on a scanning wafer. The wafers are held by a vacuum chuck and rastered by an in-vacuum motor assembly at speeds up to 105 cm/s. The jet, about 1 cm in diameter, carries a thermal power of 500 W. Test wafers (200 mm) were coated with 1.0 µm thick I-line resist and implanted with an arsenic dose of $5x10^{15}/cm^2$ at 40 keV and hard-baked at 120 °C. In our approach, the jet delivers hot, reactive species to the resist surface while the wafer temperature is held below the hard-bake temperature to prevent popping. Remarkably, it is then possible to selectively remove the crust from the unimplanted layer. Once the crust is removed, the base resist is rapidly ashed with a high temperature (low speed) scan. A light haze is formed on the wafer surface due to the reaction of atmospheric water vapor with the $As_2O_3$ particles that form during the ash process. This haze can be completely removed with a DI water rinse, after which, SEM and XPS analysis indicates no ash residues. Charge damage, interface trap density, and stress induced leakage were shown to be at or below values for the other commercial plasma ashing tools, which are known to provide damage-free ashing solutions. Silicon loss studies, in progress, will be reported at the conference. A conservative estimate of time-to-clear for a 300mm, 2-jet system is about 80s.

**PS-ThP16 Study of Tungsten Oxidation in Low-Temperature Plasma Processing**, ***S. Xu***, *L. Diao*, Mattson Technology Inc.

As the device feature size of integrated circuit continues to be scaled down, metal or polysilicon/metal stack has been used as gate electrode for transistor formation. Among different metals investigated, tungsten meets various requirements and is gradually adopted for 45nm and below nodes. However, tungsten can be oxidized easily when exposed to oxygen plasma during process, leading to degradation of device performance. One example is post-implantation photoresist stripping in oxygen plasma where tungsten oxidation results in gate profile distortion and critical dimension change. Although an effective approach to solve this problem is available by using an oxygen-free reducing gas, such chemistry usually gives a very low photoresist removal rate and poor process uniformity. The second example is selective polysilicon oxidation over tungsten after gate etching to anneal etching damage where metal oxidation is difficult to be prevented with the presence of oxygen. The current common approach is using water vapor and hydrogen mixture to do thermal oxidation, but the process requires very high temperature and tends to cause contamination issue. In this paper, a detailed and systematic work has been conducted to study the tungsten oxidation in oxygen and oxygen-containing gases in an inductively-coupled plasma reactor operating at low temperature. By using various surface analytical methodologies, the oxidation of tungsten surface has been characterized and the oxide thickness has been measured. The dependences of tungsten oxide growth or tungsten loss on various process conditions, including RF power, pressure, temperature and exposure time, and process chemistry have been investigated. The experimental results show that tungsten oxidation occurs very fast at the top surface, but the oxide growth is mostly controlled by a few process parameters. The extent of tungsten oxidation is also found to change significantly with plasma chemistry and can be varied through post-treatment. Based on this work, mechanism of tungsten oxidation in high-density plasma has been discussed. Optimized process regime and chemistry have been identified to greatly reduce or even suppress tungsten oxidation for different process applications.

**PS-ThP17 Stabilization of Ion-beam in Hall-type Plasma Processing Device**, ***F. Furukawa***, Japan Aerospace Exploration Agency

Hall-type plasma processing device, whose ionization/acceleration mechanisms are extremely same as magnetron, has great expectations as ion beam source for nano/micro processing. Plasma magneto-hydrodynamic(MHD) instability, however, causes at high-voltage mode operation of DC regime. In particular, large-amplitude instability in the tens of kHz has been a serious problem that should be solved to improve the operational stability and the device system durability. So we propose a hall-type plasma processing device with new design concepts that is capable of solving simultaneously the instability and the accelerator core overheating. The technologies for this concept are as follows: 1) To increase neutral species velocity-inlet in acceleration channel by preheating propellant at its conduit line inside accelerator system could bring about the lower amplitude. 2) This method of preheating propellant through circularly propellant conduit line inside propulsion system cools the device system, and produces the higher thrust and specific impulse with hardly changing thrust efficiency at the same time. 3) Furthermore, to select Boron-Nitride and Al2O3 as wall material of ionization- and acceleration-zone in acceleration channel respectively having different secondary-electron emission-coefficient could achieve the higher-efficiency and -durability. The hall-type beam accelerator designed using these technologies, which have high convergence and stabilization of high-power beam at a low-price, becomes a enhanced ion beam source. Verification of these reduction technologies is conducted through numerical analysisand experimental data: The dependencies of both performances (ion generation-/acceleration-efficiency/ energy-efficiency/propulsion-utilization efficiency) and instability amplitude/frequency on various parameters (discharge voltage/neutral species temperature/magnetic field profile) are estimated using unsteady numerical analysis and experimental data. Besides in order to clarify the physical mechanism of the technologies a new physical parameter ‘equilibrium length of ionization-zone’ is introduced. Also the spatiotemporal variations of plasma properties and electromagnetic field for the optimum operation are examined in the acceleration channel at the peculiar times in instability-cycle.

This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientists (A).

**PS-ThP18 Computational Investigation of Volume Discharge in a Nitrogen Laser**, *S.M. Karabanov, V.A. Korotchenko,* ***D.V. Suvorov***, Ryazan State Radio Engineering University, Russia

The laser on the basis of the second positive nitrogen system is one of the most powerful sources of UV–radiation (wave-length – 337 nanometers). The central disadvantage of a nitrogen laser obstructing to average power increase, is its low (0.1-0.3 %) efficiency. Influence of rate of interelectrode voltage rise and value peak capacity on energy of pulse radiation and pumping efficiency is investigated in the present work by means of numerical simulation for the nitrogen laser with transversely pumped and the capacitive energy storage. It is shown, that the rate increase of interelectrode voltage rise augments radiation pulse energy. It is caused by increase of the attainable overvoltage degree and energy accumulated in capacity. Simultaneously time of discharge formation and duration of impulse pumping decrease that leads to increase of radiation pulse energy. Existence of the optimum rate of interelectrode voltage rise is determined at which peak pumping efficiency is reached. At large values of rise rate the pumping efficiency decrease is explained by increase of reduced electric field intensity and primary energy input displacement from processes of excitation to ionization. On the one hand peak capacity increase leads to raise of energy entered into discharge that leads to inversion increase, and on the other hand - impulse pumping duration increases, that reduces inversion. Results of calculation show, that to increase pumping efficiency of the laser it is advisable to reduce peak capacity value at simultaneous increase of its charge voltage in order to keep its accumulated energy. The obtained results indicate the possibility of considerable increase of the nitrogen laser efficiency by providing of optimized pumping conditions.

**PS-ThP19 Ionization Comparisons Through Filtered High Power Pulsed Magnetron Sputtering**, ***S.R. Kirkpatrick***, *J. Li, S.L. Rohde*, University of Nebraska-Lincoln

Various High Power Pulsed Magnetron Sputtering (HIPIMS) voltage levels are compared in terms of their equivalent ionization potentials using a "filtered" HIPIMS source and monitoring of a pair of quartz crystal monitors. One monitor is mounted in front of the cathode; the other is mounted perpendicular to the cathode, at the end of a coil similar to those

used in filtered arc systems. A ninety degree open coil ion filter was placed 4cm from the target surface. Relative ionization rates for various applied voltages and materials are estimated through the ratio of deposition on each crystal monitor. Deposition rates for copper and titanium are observed on the "filtered" monitor both when the coil is on and off for comparison. Depositions were performed using pressures ranging from 3 to 5mTorr, and rates were found at the end of the ion filter to be more than double those of the unfiltered region. These results indicate that very high levels of ionization and directed deposition can be achieved using HIPIMS sources.

**PS-ThP20 Study of Micro-Trenching and Bowing with a Dry Etching Profile Simulator in a High-Density, Low-Pressure Plasma**, *J. Saussac, J. Margot,* Université de Montréal, Canada, *M. Chaker*, INRS, Canada

Sub-micron technologies are crucial for present and future communication systems. The complexity of device fabrication processes requires a deep understanding of the fabrication issues, especially when dealing with new materials and complex device geometry. Plasma etching is one of the necessary tools to realize such devices. Numerical simulations are of great interest for providing insights into the physics underlying plasma etching processes and are therefore helpful for optimizing the experimental conditions. In this work, we propose a 2-dimensional plasma etching simulator. According to our cellular approach, each cell is characterized by its state, namely etched, unetched, mask, mask surface and material surface. This state evolves according to the interaction between the cell and the incident particles. Monte-Carlo methods are used to define particle trajectories and the nature of interacting particles (ion or neutral). The etched profiles achieved from our numerical simulations favorably compare with those corresponding to various experimental conditions (physical sputtering, ion-assisted etching, mask geometry and angular ion distribution) as found in the literature. In particular, micro-trenching and bowing of the side-wall for Si and $SiO_2$ are observed. The validation of our numerical approach through this comparison enables us to further apply it for more complex materials of interest for photonic applications, such as $VO_2$ and $SrTiO_3$. The next step in this study will be to examine the role of plasma parameters on the etching characteristics of such materials, in order to optimize profile accuracy (low micro-trenching, low bowing and large aspect ratio).

**PS-ThP21 Effect of a High Negative DC Bias Voltage Applied on an Electrode Immersed in an Inductively Coupled Plasma**, *A. Ranjan,* University of Houston, *L. Chen,* Tokyo Electron U.S. Holdings, *D.J. Economou, V.M. Donnelly*, University of Houston

A biased electrode immersed in a plasma has been used to control the plasma parameters by various researchers. For example, Coburn and Kay[1] and Xu et al[2] inserted a separate positively biased electrode into a plasma, to control the plasma potential, and the energy distribution of ions extracted from the plasma. Here, we report the effects of applying a high negative DC bias voltage on an electrode immersed in an inductively coupled plasma. Plasma properties with the DC voltage ON and OFF were measured using a Langmuir Probe. Superposition of a high negative DC voltage was found to change the electron energy distribution function (EEDF) and the plasma density significantly. Plasma density increased by 25%-250% by the application of high DC voltage of -900 V at 100 mTorr and rf power of 2000-800 W. These changes can have dramatic effects on plasma chemistry. It is expected that this imposed DC bias technique will provide an additional variable to control the etch rate and pattern profile in microelectronics fabrication.

[1]J. W. Coburn and E. Kay, J. Appl. Phys., 43, 4965 (1972).
[2]L. Xu, D. J. Economou, V. M. Donnelly and P. Ruchhoeft, Appl. Phys. Lett., 87, 041502 (2005).

**PS-ThP22 Planar Laser-Induced Fluorescence Measurements in an Inductively Coupled Plasma Reactor**, *B. Jacobs, W. Gekelman,* University of California - Los Angeles, *M. Barnes,* Intevac Corporation, *P. Pribyl*, University of California - Los Angeles

Planar Laser-Induced Fluorescence (LIF) measurements of ion velocity distribution functions have been made in an inductively coupled plasma reactor with a pulsed plasma source. Vertical and radial velocities have been measured at thousands of spatial locations within a plane, and the LIF data has been calibrated to a 96 GHz microwave interferomter. The ion behavior in the presheath region above the wafer is investigated in particular.

**PS-ThP23 Exotic Shapes of Gold Nanoparticles Synthesized with Plasma in an Aqueous Solution**, *J. Hieda, M. Oda, N. Saito, O. Takai*, Nagoya University, Japan

Plasma materials processing in liquid phase has a potential of an industrial process for metal nanoparticles since this process would realize extremely rapid reaction under a high pressure. Moreover, this method does not require a reducing agent to fabricate metal nanoparticles from the solution containing metal ion and extraction process of residues. In our previous study, gold nanoparticles were successfully synthesized with discharge in an aqueous solution. In this study, we reported the shape change of the nanoparticles fabricated with discharge in the aqueous solution. In order to obtain various shapes of nanoparti1cles, the amount of additives in the solution was changed. Gold nanoparticles were synthesized through reduction with a discharge in the aqueous solution containing chlorauric acid as metal source. Gelatin was added to the aqueous solution as a stabilizer. Electric conductivity of the solution was varied from 500 to 2500 μS/cm in order to obtain suitable condition for generation of discharge by the addition of KCl. The discharge was generated by a pulsed power supply. The applied voltage and the pulse width were ca. 1600 V and 2 μs, respectively. The gold nanoparticles were observed by transmission electron microscopy (TEM) and analyzed by energy dispersive X-ray spectroscopy (EDS). Plasmon band of the gold nanoparticles were measured by ultraviolet-visible spectroscopy (UV-Vis). TEM images show the presence of exotic shapes of gold nanoparticles, that is, triangle sheet, pentagon, hexagon and so on. The exotic shapes were generated when the concentration of KCl became higher. The synthesis of nanoparticles using other surfactants (e.g. CTAB) with discharge was also demonstrated. These results suggested that the shapes of the nanoparticles strongly depend on KCl or surfactant concentrations in the solution.

**Plasma Science and Technology**

**Room: 606 - Session PS-FrM**

**Plasma-Surface Interactions III**

**Moderator:** E.S. Aydil, University of Minnesota

8:00am **PS-FrM1 Controlling Surface States of Nanocrystalline TiO2 and its Application in Dye-Sensitized Solar Cells**, ***M. Dhayal***, National Physics Laboratory, India, *H.B. Gu, K.H. Park*, Chonnam National University, Korea

Plasma surface modification and weak acid treatments of nanocrystalline TiO2 has been carried out to improve efficiency of dye sensitized solar cells (DSSC). The argon ions in low pressure gas discharge can modify the TiO2 surface chemistry and had increased in the proportion of Ti3+ surface states. The proportion of different surface functionalities such as alcohol/ether (C-OX), carbonyl (C=O) and C(=O)OX were also significantly changed. Similarly the acid treatment of TiO2 had also change the surface chemistry. In this study the relative change in the surface chemistry with these two different methods has been discussed. These treatments have advantages for the adsorption to dye molecules and enhancement of the photoelectric performance of DSSC. The improvement in the energy conversion efficiency of dye-sensitized solar cells (DSSCs) with controlled surface states had been investigated.

8:20am **PS-FrM2 Role of UV/VUV Radiation and Ion Bombardment in the Degradation and Roughening of Photoresist Polymers**, ***D.G. Nest***, *D.B. Graves*, University of California, Berkeley, *S. Engelmann, R.L. Bruce, T. Kwon, R. Phaneuf, G.S. Oehrlein*, University of Maryland, College Park, *C. Andes*, Rohm and Haas Electronic Materials, *E.A. Hudson*, Lam Research Corp.

This study focuses on the relative roles of rare gas ion bombardment and UV/VUV radiation in photoresist (PR) polymer degradation during plasma etch and pattern transfer. We present results of a collaborative study of PR etching and roughening of current generation methacrylate-based 193 nm PR polymers and 248 nm PR. Independently controlled ion and UV sources in a vacuum beam system are used to simulate plasma-photoresist interactions, and the relative importance of UV/VUV radiation and ion bombardment during plasma etch are elucidated. The effects of ion bombardment tend to be concentrated in the near-surface layer. All PR polymers under ion bombardment appear to form a highly cross-linked near-surface layer. By contrast, the effects of UV/VUV radiation, as characterized by transmission Fourier Transform Infrared (FTIR) Spectroscopy, penetrate deeper into the bulk polymer and are more sensitive to the chemical composition of the PR polymer. Surface roughness and morphology depend on the composition of the PR as well as the ion bombardment and UV/VUV exposure protocol. Differences in polymer chemistry are correlated to surface morphological changes. Results from the vacuum beam experiments are compared to measurements made on PR exposed in plasma reactor experiments.

8:40am **PS-FrM3 About the Surface Roughness Generated by Plasma Etching Processes**, ***M. Martin***, *G. Cunge*, CNRS/LTM, France

As the critical dimension of the features decrease for each new generation of CMOS transistors, the thickness of the layers being etched also decreases. When the thickness of the layer approaches 10 nm, a new problematic is emerging: the roughness generated by the plasma etching process could become comparable to the thickness of the layer being etched potentially causing selectivity issues. In this work, we have systematically analyzed the roughness generated in c-Si (100) and in p-Silicon when etched in high-density plasmas over a wide range of conditions (pressure, rf power) using $SF_6$, $CF_4$, $Cl_2$ and HBr chemistries. The roughness is characterized by AFM. In this work, we demonstrate unambiguously that high-density HBr and $Cl_2$ plasmas DO NOT generate roughness during etching but on the contrary tend to smooth the existing surface roughness if already present. By analyzing the time evolution of the shape of self organised silicon nanopilar (patterned using diblock-copolymers), we show that the smoothening properties of etching plasmas is due to shadowing effects : the "hills" receive a high radical flux than the "valley" and are thus etched faster. In contrast, F-based plasma generates a significant surface roughness whose amplitude increases with the etching time. However, we show that the roughness formed in these conditions is generated by micromasking of silicon by $AlF_x$ particles generated by the sputtering of the ($Al_2O_3$) reactor walls. A high percentage of Al is indeed detected on the surface after etching in F-based plasmas. As a matter of fact when the chamber walls are intentionally coated by a carbon layer prior to the silicon etching process (thus preventing Al sputtering), the F-based plasmas behave like the other etching chemistries investigated: they rapidly smooth any existing roughness.

9:00am **PS-FrM4 Influence of Plasma Etch Processing Parameters on Morphological and Topographic Transformations of Advanced Photoresist Materials**, ***S. Engelmann***, *R.L. Bruce, T. Kwon, R. Phaneuf*, University of Maryland, College Park, *C. Andes*, Rohm and Haas Electronic Materials, *D.G. Nest, D.B. Graves*, University of California, Berkeley, *E.A. Hudson*, Lam Research Corp., *G.S. Oehrlein*, University of Maryland, College Park

Plasma based transfer of photoresist (PR) patterns into underlying substrates is basic to micro- and nano-fabrication, but suffers from problems like introduction of surface and line edge roughness in the PR/underlying features as a result of plasma processing. In this collaboration, we seek to develop a deeper understanding of the influence of both PR materials and plasma parameters in introducing undesirable changes in PR blanket films and nanostructures. Etch rates, chemical and morphological evolution of fully formulated PR systems as well as carefully selected model polymers have been studied along with a set of sub-micron sized patterned structures using ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, and secondary electron microscopy. The current work is designed to complement prior studies on the temporal evolution of plasma-induced PR modifications for a set of different materials processed over a limited plasma parameter range. Using an Inductively Coupled Plasma (ICP) source, a survey of the effects of bias power and voltage, source power, pressure, and feed gas composition ($C_4F_8$/% Ar) on 193 nm PR etching behavior and surface modifications has been undertaken. For comparison, PR modifications using discharges based on $CF_4/H_2$ mixtures were studied as well. The pure $CF_4$ discharge resulted in a relatively smooth top surface due to high removal rates. But excessive lateral etching caused tapered feature profiles. On the other hand, $CF_4$ discharges admixed with $H_2$ to improve the profile resulted in smooth top surfaces combined with low removal rates similar to $C_4F_8$/90% Ar. We also will present results of changes in line edge and width roughness for actual PR nanostructures, and compare these with data obtained using blanket PR films exposed using the same plasma operating conditions.

9:20am **PS-FrM5 Effect of Charging on Twisting of Extremely High Aspect Ratio Features in Plasma Etching***, ***A. Agarwal***, University of Illinois at Urbana-Champaign, *M.J. Kushner*, Iowa State University

The plasma etching of extremely high aspect ratio features (eHAR) provides challenges to maintain critical dimensions. As aspect ratios approach and exceed 100, undesirable behaviors have been observed, such as extreme tapering and twisting of features. Twisting is the sometimes sudden turning of a via or trench from the vertical to a side angle. These behaviors often occur randomly. For example, of three adjacent features, only one may display the behavior. The behaviors are also sometimes associated with location on the die, such as near an open area, or location on the wafer, being more likely near the edge of the wafer. Current theories on the source of twisting and errant behavior focus on charging effects, anisotropic ion energy distributions and the randomness of the composition of the ion and radical fluxes as the opening of the feature approaches only a few tens of nm. In this talk, processes leading to twisting of eHAR features in polymerizing (etching of $SiO_2$ in fluorocarbon plasmas) and in non-polymerizing (etching of Si in chlorine plasmas) chemistries will be discussed using results from a computational investigation. The Monte Carlo Feature Profile Model (MCFPM) was modified to include the effects of charging by electrons and ions, including solution of Poisson's equation and conduction current through solid materials. We found that twisting largely results from a confluence of factors, including trapping of charge in polymer, randomness in the neutralization of charge due to the stochastic-like current that enters small features and location of the feature on the die. For example, trenches adjacent to open areas are influenced by charging in the open field, an effect that diminishes with distance from the open field. The twisting effects are generally diminished but not eliminated with increasing voltage.

*Work supported Micron Technology Inc., Semiconductor Research Corporation and the National Science Foundation.

9:40am **PS-FrM6 Role of Additives (O2, CO and CO2) in NF3 Remote Plasma Etching of Si3N4**, ***J.J. An***, *H.H. Sawin*, Massachusetts Institute of Technology

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. It is found that less than 5% of additives such as O2, CO and CO2 in NF3 plasma enhance silicon nitride etching rates particularly at lower temperatures. Using line-of-sight mass spectrometry, we have measured the atomic fluorine density and shown than it is not significantly altered by the additives. While nitric oxide (NO) generated in plasma is considered to be the main contributor of the enhancement of etching rate, its measured levels are small. Besides NO, the role of carbon containing gas products is also taken into account. 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 flow rates, pressure and sample temperature.

10:00am **PS-FrM7 Measurement of Modified Layer Formation of 193 nm Photoresist during Short Time Plasma Exposure**, ***M. Sumiya***, Hitachi High-Technologies Corp., Japan and University of Maryland, *R.L. Bruce, S. Engelmann, F. Weilnboeck, G.S. Oehrlein*, University of Maryland

The degradation of photoresists (PR) during plasma etching is one of the issues for nanoscale-fabrication. Although it has been already reported that surface roughness develops within a few seconds plasma exposure and leads to striations,[1] the mechanism of surface roughness formation during the initial stages of plasma exposure is not well understood. In this study we employed a shutter approach[2] to achieve rapidly steady-state plasma condition for processing PR surface. The time-evolutions of optical constants and thickness of the modified layer on the PR surface were obtained using 2 layer optical modeling of the ellipsometric data. The change of surface composition was observed by X-ray photoelectron spectroscopy (XPS). Remarkable differences of the etch behavior during the early etch period for different discharge conditions, i.e., ion energy, pressure and stage temperature, were observed. We found that the modified layer is formed within a few seconds and a steady-state modified layer is subsequently seen. It was revealed that these differences of etch behavior for different etch condition at the earlier etch period are due to difference of fluorination degree of the PR surface and having higher etch rate under low fluorination leads to rough surface. We also compared the etch behaviors of 193 nm PR and 248 nm PR materials. Whereas for 193 nm PR etching was observed immediately, for 248 nm PR, fluorocarbon film deposition took place at first until a fluorinated surface developed. The reason for different etch behavior of both PRs is the high oxygen content of 193 nm PR relative to that of 248 nm PR. Oxygen enhanced the etching rate of 193 nm PR during early plasma exposure when the surface roughness is introduced. Additional details on the relationship of the initial surface condition and formation of rough surface for PR materials will be discussed.

[1]X. Hua et al., J. Vac. Sci. Technol. B24(4)(2006)1850.
[2]G. S. Oehrlein, et al., J. Vac. Sci. Technol. B24(1)(2006)279.

10:20am **PS-FrM8 A Study on the Oxidation Properties of W Surface by $O_2$ Plasma and Reduction of $WO_x$ Layer by $H_2$ Plasma in Sub 50nm Patterning Process**, ***J.K. Kim***, *B.S. Kim, S.S. Jeong, T.H. Ahn*, Samsung Electronics, South Korea

As the feature size gradually shrinks down to nano scale of sub 50nm, various metals like as W, Ti, and Co, have been introduced as a low resistance material for word line. Recently, W has become to the most powerful candidate and widely used for several applications. For the formation of W pattern, the most challenging problem is the oxidation of W surface. Generally, we treat wafer with $O_2$ plasma to remove the organic mask layer and polymeric residues after W etching process. W surface is oxidized to $WO_x$ layer by reactive oxygen radicals during plasma ashing. The oxidation of W surface brings increase of pattern resistance and variation of critical dimension. In this study, we controlled the reactivity between W surface and oxygen radical varying process parameters such as radical flux, RF power and especially electrode temperature. Also, we characterized the W surface using XRR, SFX and checked the change of line resistance to compare the oxidation amount. Oxygen radicals activated moderately, could not react with W surface, while organic polymer could be sufficiently removed. Using properly activated oxygen radical, we can find the reasonable process window which is nearly free from surface oxidation and polymeric residues. Even though we find the optimum process condition, there are still thin $WO_x$ layer after ashing. In order to remove this layer, we also investigated post treatment process using $H_2$ containing plasma. We found that hydrogen radical allowed a quick recovery of $WO_x$ layer to their initial state of W. Finally, we proposed a multi-step plasma treatment process to keep W surface from oxidation during plasma ashing.

10:40am **PS-FrM9 Model Analysis of the Ion Reflection on Surfaces and the Profile Evolution during Etching of Si in Chlorine- and Bromine-Containing Plasmas**, ***S. Irie***, Kyoto University, Japan, *M. Mori, N. Itabashi,* Hitachi Ltd.,Japan, *K. Eriguchi, K. Ono*, Kyoto University, Japan

In the profile evolution during plasma etching, the reflection of energetic ions on feature sidewalls is appreciated to be important to cause profile anomalies near the feature bottom such as footing and microtrenching. We have developed a model for the feature profile evolution of Si etching in chlorine- and bromine-containing plasmas. The model incorporates an atomic-scale cellular model of surface reaction layers and Monte Carlo calculation for the trajectory of ions on feature surfaces, including their reflection on and penetration into surfaces. The model takes into account the formation of surface reaction multilayers caused by adsorption of neutrals and penetration of ions, deposition of etch products and by-products, and surface oxidation. This paper presents an investigation of effects of the energetic ion scattering on Si surfaces. In the model, the collision between ions and Si atoms on surfaces is assumed to occur, when the impact parameter is smaller than the cutoff radius; the trajectory of ions is analyzed by the Monte Carlo calculation, based on the momentum and energy conservation for an incident ion through successive two-body elastic collisions with substrate Si atoms. The impact parameter and scattering angle are calculated at each collision in the three-dimensional space. The interaction potential of Si ion is necessary for calculation, and the existing classical potential or Stilling-Weber potential is employed for the potential of Si-Cl. However, the potential of Si-Br is not well known, and so to determine the potential function for Si-Br systems, we perform ab initio quantum chemical calculations based on a density-functional method using Gaussian. Then, we analyze the scattering of $Cl^+$ and $Br^+$ ions on Si surfaces based on their potential calculated, showing that there is a difference of the scattering on Si surfaces between $Cl^+$ and $Br^+$ ions. Compared the scattering of $Br^+$ ions with that of $Cl^+$ ions, the number of $Br^+$ ions reflecting from Si substrates is small for all incident angle, the distribution of reflection angles is narrow, and the kinetic energy loss is rather large. The difference of the scattering on Si surfaces is attributed not only to the potential, but also to the masses of atoms. The profile simulation during etching in HBr plasmas, using the potential for Si-Br calculated, is compared with the experiments, to examine the effects of ion reflection on feature surfaces.

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