Monday Morning, October 31, 2011

Energy Frontiers Focus Topic
Room: 103 - Session EN+PS-MoM

Plasmas for Photovoltaics & Energy Applications
Moderator: S. Agarwal, Colorado School of Mines

8:20am EN+PS-MoM1 Plasma Energy R&D at National Fusion Research Institute (NFRI): Fusion Energy, Silicon Quantum Dot Solar Cell, and Plasma-Enhanced Coal Gasification, *S.J. Yoo*, National Fusion Research Institute, Republic of Korea **INVITED**
National Fusion Research Institute (NFRI) is a unique national laboratory dedicated to conducting research and development of the most powerful plasma energy application, the fusion energy, in Korea: We have constructed and a fully superconducting Tokamak device named KSTAR (Korea Superconducting Tokamak Advanced Research) which is now successfully in operation, and actively involved in the world's largest joint fusion project - International Thermonuclear Experimental Reactor (ITER), in which seven countries are participating to investigate engineering feasibility of fusion power commercialization.

Besides the fusion research, the NFRI has actively developed various plasma applications related to energy harvesting such as silicon quantum dot solar cells and plasma-enhanced coal gasification.

We have challengingly developed a new fabrication method of the silicon quantum dot solar cell by using hyperthermal neutral beams which are neutral beams with an energy range of 1 ~ 100 eV and very effective tools for thin film deposition at much lower substrate temperature without plasma-induced damages. The hyperthermal neutral beams can be effectively applied to each fabrication step of the silicon quantum dot solar cells: Deposition of a silicon thin film consisting of nano-crystal silicon and amorphous silicon matrix, then selective etching of the amorphous silicon matrix by keeping only nano-crystal silicon remained in order to obtain the silicon quantum dots, thereafter dielectric barrier coating on the silicon quantum dot surface, and then repetition of the procedure until a required thickness achieved.

We also have developed a steam plasma torch driven by microwave powers of 2.45 GHz and 915 MHz for effective gasification of various hydrocarbon materials and even low grade coals which can be hardly gasified by conventional thermal gasification methods since the steam plasma torch can produce much more abundant reaction catalysts such as O*, H*, OH*, H_2O_2, and O_3 than the thermal gasification methods. And, furthermore, the microwave plasma torch has a great advantage of the system life time compared to conventional arc plasma torches for which metallic electrodes are inevitable and thus easily eroded by the reaction catalysts produced for the coal gasification.

9:00am EN+PS-MoM3 Synthetic Fuel Processing through Plasma-Assisted CO_2 Conversion, *S. Welzel*, S. Ponduri, F. Brehmer, M. Creatore, M.C.M. van de Sanden, R. Engeln, Eindhoven University of Technology, Netherlands
Continuously increasing green house gas emissions and forthcoming (fossil) fuel depletion has stimulated research in novel fuel processing, cleaner combustion as well as CO_2 capturing and conversion. Conventional fuel processing usually aims at producing syngas (CO/H_2) mixtures that may be further converted into value-added hydrocarbons and oxygenates ($C_xH_yO_z$). Photocatalytic CO_2 hydrogenation is now considered as alternative approach which would simultaneously lead to a global green carbon cycle. It could reduce atmospheric CO_2 concentrations, while at the same time provide fuels on a renewable basis that can directly be supplied to our present energy infrastructure. Since the efficiency of such an artificial photosynthesis is low, we propose the plasma-assisted hydrogenation of CO_x into hydrocarbons.

This contribution focuses on the efficiency of CO_2 depletion and selectivity of CH_4 production in a low-temperature plasma expansion. The plasma is created from mixtures of argon and hydrogen while CO_x is injected into the expansion part where the dissociation mechanism might be radical- and/or ion-driven. Results on measurements of the (steady state) gas composition obtained by mass spectrometry and mid-infrared tuneable diode laser absorption spectroscopy will be reported.

Especially under argon rich conditions, where the chemistry is mainly driven by combined charge exchange with the Ar ions and dissociative recombination, a CO yield of 50 % was achieved. CH_4 formation was particularly detected at high hydrogen admixtures. C_2H_y hydrocarbons were in most cases absent while H_2O and CO turned out to be the main stable products. The results suggest an inherent syngas step during the plasma-assisted conversion approach, particularly a successive hydrogenation of CO.

9:20am EN+PS-MoM4 Effective Light Trapping for Crystalline Silicon Solar Cells by Plasma Texturing, *F.M.M. Souren*, Eindhoven University of Technology, Netherlands, *J. Rentsch*, Fraunhofer Institute for Solar Energy Systems (ISE), Germany, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands
Currently, in the photovoltaic (PV) industry, wet chemistry based etching is used for saw damage removal and surface texturing. It is known that plasma based dry etching leads to an improved light trapping on multi-crystalline silicon material and, therefore, it has the potential to increase the solar cell efficiency. However, up to now plasma based texturing has not been implemented in the PV industry, because of the very low etch rate (<1 μm/min) and the high cost of ownership. In this study, different front surface textures obtained by means of the Linear Microwave Plasma (LMP, commercialized by Roth&Rau) technique and the high rate Expanding Thermal Plasma (ETP, commercialized by OTB-Solar) technique, are investigated to reduce the overall reflection losses of mono-crystalline silicon solar cells and compared to KOH/IPA (Potassium hydroxide/Isopropanol) which is the standard process in solar cell manufacturing industry. The created textures employing the different etching techniques are characterized by reflectometry (250-1200 nm) to determine the weighted reflection and by Atomic Force Microscopy (AFM) to measure the surface topography so as to determine statistical roughness parameters. We have found that the average scatter angle, determined from the AFM measurements, shows a clear correlation to the measured weighted reflection. Effective light trapping has been obtained for two typical textures based on the described etching techniques. A texture which leads to a successive hit of the incident light ray towards the solar cell surface, can result in effective light trapping, as for example, the KOH/IPA process which creates a pyramidal texture. Efficient light trapping can also be obtained by the creation of a diffuse front surface (resembles the topography of "black silicon"), as for example by using the LMP technique, under the conditions used, which creates micro roughness. This micro roughness can be described as an effective medium with a refractive index between air and silicon and a typical thickness of up to (60±10) nm [1]. The micro roughness leads to an effective light trapping of a broad range of wavelengths from 250 nm up to 1200 nm. The light trapping of the wafer etched by the ETP technique is smaller than the as cut wafer and can be explained by a smaller average scatter angle compared to the as cut wafer. A short post treatment of the ETP textured wafer by the LMP technique, creates a diffuse front surface and results, therefore, in an improved light trapping. Moreover this combination shows great promise for a cost-effective approach towards plasma based texturing.

[1] R.B. Stephens and G.D. Cody, Thin Solid Films 45 (1977) 19.

9:40am EN+PS-MoM5 RF-PECVD Processes Excited by Asymmetric Voltage Waveforms, *P.-A. Delattre*, S. Pouliquen, Laboratoire de Physique des Plasmas, France, *E.V. Johnson*, Laboratory of Physics of Interfaces and Thin Films, France, *J.-P. Booth*, Laboratoire de Physique des Plasmas, France
Voltage Waveform Tailoring (VWT) is a promising new technique for Radio-Frequency (RF) process plasma excitation. It is known that asymmetric waveforms resembling *peaks* (short positive and long negative voltage) or *valleys* (long positive, short negative voltage) can produce a voltage self-bias, even in a symmetrical reactor [1], known as the Electrical Asymmetry Effect (EAE). We have implemented a system to provide such voltage waveforms on the RF electrode of our Capacitively Coupled Plasma (CCP) reactor. For a peak to peak voltage (V_{PP}) of 300 V, we can control the self-bias from -190 V to 15 V, without changing any other process parameter. A new differential RF probe gives us the real-time current and voltage derivatives, and therefore, the instantaneous power. For a voltage waveform composed of a 15 MHz fundamental and three harmonics, instantaneous power changes from +1 kW to −1kW in 10 ns. Using a hairpin resonator probe in hydrogen at 13 Pa, we have measured an electron density of 2E8 cm^{-3} with a standard sine waveform, 2E9 cm^{-3} with a valleys waveform and 2E10 cm^{-3} with a peaks waveform (all with V_{PP}= 300V). With a view towards photovoltaic applications, using a gas mixture of 4 % of SiH_4 in H_2 at 65 Pa, we have achieved a deposition rate of high-quality amorphous silicon of 1 Å/s for sine, 2.7 Å/s for valleys, and 3.8 Å/s for peaks voltage waveforms.

[1]Brian G Heil *et al* 2008 *J. Phys. D: Appl. Phys.* **41** 165202

10:00am EN+PS-MoM6 Spontaneous and High Rate Synthesis of Nanocrystalline Silicon by Expanding Thermal Plasma, *İ. Doğan, NJ. Kramer, M.A. Verheijen,* Eindhoven University of Technology, Netherlands, *K. Dohnalova, T. Gregorkiewicz,* University of Amsterdam, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Silicon nanocrystals (Si-NCs) draw attention since they exhibit size dependent luminescence, improved charge storing capacity and increased surface reactivity. For instance, the size dependent optical properties of Si-NCs show great promise for increasing the efficiency of solar cells. Si-NCs could be used as spectrum down converters by converting the excess energy of a hot photon to generate multiple exciton pairs. For successful applications, the main issues on Si-NC synthesis are size control and surface engineering for improved optical properties, and high throughput. Among these points, the amount of throughput is highly critical for large scale applications however, it is not possible to achieve with current production techniques. Our research goal is to show that it is possible to fulfill these demands with a novel route by using the remote expanding thermal plasma (ETP) technique. Synthesis of Si-NCs in a remote Ar/SiH$_4$ plasma occurs by means of a reaction sequence of ion-SiH$_4$ charge exchange and subsequent addition of SiH$_4$ molecules. This realizes spontaneous and nearly complete conversion of SiH$_4$ into Si-NCs with very high throughputs of about 25mg/min, the fastest deposition rate reported in the literature so far. Moreover, ETP has the freedom of tuning the size of the Si-NCs by controlling the flow rates of SiH$_4$ and Ar, i.e. the residence time in the plasma. Synthesized Si-NCs have a bimodal distribution of small (4-7nm) and large (50-80nm) sizes as confirmed by TEM, which is a consequence of the plasma expansion and reactor geometry. Bimodality has been analyzed with Raman spectroscopy by studying the asymmetry and shift in the transverse optical vibration mode of bulk-Si at 521cm^{-1}. Photoluminescence spectroscopy confirms the presence of monodisperse size distribution of small Si-NCs (4-7nm) leading to luminescence in the region 600-900nm. Observation of luminescence illustrates the quality of the nanocrystal surface passivated by the rapid native oxidation. Preliminary results show separation of the bimodal distribution can be controlled by means of geometrical isolation of the regions, in which small and large particles are formed.

10:40am EN+PS-MoM8 SiH$_4$ and SiF$_4$ Dissociation in Matrix Distributed ECR Sources, and Potential for High Deposition Rate of Thin Film Silicon Alloys, *S. Kasouit*, Total S.A, France, *P. Bulkin, P. Roca i Cabarrocas*, LPICM, France

Depositing at high rates and on ever larger areas are important objectives for the reduction of thin film silicon modules costs. High deposition rates have been achieved so far using different plasma sources but uniformity over large areas is still problematic. Matrix distributed electron cyclotron resonance (MDECR) systems consist of individual ECR plasma sources, which can be arranged in arrays with virtually no size limitations. Deposition rate of silicon alloys exceeding 10 nm/s, has been demonstrated, but little is known so far about the precursors' dissociation and species fluxes onto the surface.

We study here the dissociation of Silicon film precursors, using optical emission spectroscopy and quadrupole mass spectrometry, both in the plasma phase and in the fore line. We correlate the dissociation on the one hand to the electron density and temperature measured using Langmuir probes and microwave interferometry, and to film growth rate and structure on the other.

It is found that more than 90% of SiH4 is used across a wide range of microwave powers, with a small dependence on gas residence time and pressure. Deposition rate depends primarily on the total flow of SiH4, and values above 3 nm/s are easily obtained. Transition from amorphous to microcrystalline silicon growth, on the other hand, occurs at high powers, and correlates to the electronic temperature and the high H/Si ratio observed in the gas phase. Direct dissociation of SiH4 by electron impact, followed by deposition from atomic Si and subsequent crystallization by hydrogen is therefore a satisfactory explanation.

On the contrary, for deposition from SiF4 , consumption is found to be lower than 60%, and independent of the gas residence time and microwave power. The deposition rate is also much lower, on the order of 0.3 nm/s. SiF4 consumption increases with the total hydrogen flow rate added to the mixture. The total concentration of atomic Si in the gas phase varies linearly with the product of SiF and H species, estimated by actinometry, suggesting fluorine abstraction by hydrogen as a possible mechanism. Deposition rate is also proportional to the Si content in the plasma phase and increases with the hydrogen flow rate added to the plasma. We propose that film growth from MDECR plasmas of SiF4/H2 mixtures occurs through the deposition

of atomic silicon, obtained from hydrogen abstraction of fluorine in the gas phase, direct electron impact dissociation of SiF4 playing a smaller role.

This illustrates the importance of gas phase reaction for achieving high deposition rates, even in the case of high density low pressure plasma sources.

11:00am EN+PS-MoM9 The Effects of Showerhead Hole Structure on the Deposition of uc-Si:H Thin Films by VHF PECVD, *S.-S. Wi, Y.-G. Kim, H.-J. Lee,* Pusan National University, Republic of Korea, *D. Kim, D. Hwang, W.S. Chang*, LG Electronics, Republic of Korea

We presents the characteristics of hydrogenated microcrystalline silicon thin films deposited from SiH$_4$/H$_2$ in 40 MHz plasma enhanced chemical vapor deposition (PECVD)equipped with multi-hole-array showerhead. The effects of hole array structure are analyzed in terms of their diameter and depth. Cross dependences between the hole structure and process parameters, such as SiH$_4$ concentration, rf power, pressure, substrate temperature and total gas flow rate, are also investigated. The results show that deposition rate is not a strong function of hole structure compared with other process parameters. However, it is found that uniformity can be controlled by varying the surface density of hole array. With decreasing total flow rate, faster increase in deposition rate is found at the multi-hole array compared with flat electrode. This may be attributed to the high electron density and longer residence time of within the holes. It is demonstrate that the multi hole array electrode can be used as an effective control variable for optimization of Si thin film solar cell PECVD process.

11:20am EN+PS-MoM10 Plasma-Enhanced CVD and ALD Prepared Nanolayers for High-Efficiency Solar Cell Manufacturing, *W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands **INVITED**
Photovoltaics has become a very innovative field of research and manufacturing due to the continuous improvement in the solar cell cost/performance ratio and its tremendous growth opportunities (past average annual growth rate of 40%). Several innovations with respect to the improvement of the cell efficiency lie in the field of thin film technology, not only for thin-film solar cells but also for crystalline silicon solar cells which are currently still dominating the market (87% market share in 2010). One particular trend is the application of ultrathin films or "functional nanolayers" for solar cell interface engineering. In crystalline silicon technology these nanolayers have as a main application the reduction of charge carrier recombination at interfaces through "surface passivation". Plasma-based deposition processes such as plasma-enhanced chemical vapor deposition (CVD) are key for the preparation of such films and recently the interest also shifted to (plasma-enhanced) atomic layer deposition (ALD) processes due to their precise growth control and their excellent uniformity and conformality [1]. Moreover, ultrathin films of < 10 nm have been found feasible in terms of reaching very-well passivated surfaces. In this contribution, the application of ultrathin films of various materials such as a-Si:H, a-SiN$_x$:H, SiO$_2$, and in particular Al$_2$O$_3$ will be addressed. The preparation methods will be described as well as the relevant surface reaction mechanisms during the film synthesis. Passivation and solar cell results will be presented with a main emphasis on the key mechanisms underlying the good passivation performance of the ultrathin films. Also the market feasibility of new ALD technologies, e.g., in terms of high throughput processing, will be addressed.

[1] Atomic layer deposition: prospects for solar cell manufacturing, W.M.M. Kessels, et al., Proc. 33rd IEEE Photovoltaic Specialist Conference, San Diego, U.S.A. (2008).

Plasma Science and Technology Division
Room: 201 - Session PS-MoM

Advanced FEOL / Gate Etching I
Moderator: A. Agarwal, Applied Materials, Inc.

8:20am PS-MoM1 Impact of Synchronized Plasma Pulsing Technologies on Key Parameters Governing STI Etch Processes, *M. Haass*, M. Darnon, G. Cunge, P. Bodart, C. Petit-Etienne, M. Brihoum, L. Vallier,* LTM-CNRS, France, *S. Banna,* Applied Materials, Inc., *O. Joubert*, LTM-CNRS, France
Plasma etch processes are the only technological solution to address the critical dimension control at the nanometer range imposed by the continuous downscaling of CMOS device dimensions in microelectronics.

* Coburn & Winters Student Award Finalist

However, the current processes are reaching their limits of controlling etch selectivity, defects, critical dimensions and uniformity. Lately, pulsed plasmas are increasingly used to overcome some of these limitations. On the basis of HBr/O_2 plasmas, dedicated to STI (Shallow Trench Isolation) etching, we discuss the role of the pulse parameters regarding the etched profiles, the reactive etch layer, the uniformity and the passivation layer. To investigate the passivation layer at various trench depths and CDs we developed a new XPS technique for quasi in-situ chemical topography analysis.

The experiments are carried out in a 300 mm AdvantEdge™ tool from Applied Materials Inc. The two generators to sustain the plasma (ICP) and to polarize the wafer (CCP), operated at 13.56 MHz, have been modified with the Pulsync™ system to allow pulsing at a wide range of parameters. However, only synchronous pulsing is studied here. Moreover, a Theta300 angle resolved XPS system from Thermo VG is connected under vacuum, allowing quasi in-situ analysis of an etched sample. Several additional diagnostic methods including time resolved UV-absorption, mass spectroscopy and ellipsometry are used to study the impact of pulsing the plasma on the surface and the gas phase compared to a continuous wave process.

We demonstrate that plasma pulsing can minimize the mask faceting and consumption which is due to a change in the ion energy distribution and the presence of larger molecular ion species. The duty cycle controls the formation of the passivation layer that governs in turn the form of the etched profiles. This correlation can partly be explained by less dissociated oxygen molecules in low duty cycle pulsing. Nevertheless, XPS analyses show that the chemical composition of the passivation layer changes little with height and trench CD while its thickness is directly linked to the aspect ratio of the analyzed part of the sidewall. Less thickness variation with respect to the aspect ratio is observed in pulsed mode, which explains an improved local uniformity in profile evolution. Furthermore, the time compensated etch rate with respect to the actual ON time of the plasma is increasing at low duty cycles due to a change of etch regime from more radical flux limited to ion flux limited. Nevertheless, the overall process etch rate is decreasing in pulsed mode which can be partly counteracted by increasing the source and the bias power.

8:40am **PS-MoM2 Effect of Si Damage on Shallow Source-Drain (SSD) Recess Structures**, *J. Guha*, *S. Sriraman*, Lam Research Corporation
Continued scaling in the semiconductor industry provides new challenges for critical Front-end-of the-line (FEOL) process etch applications in front-end logic devices. One such application that is utilized in the PMOS transistor is the Strained Source Drain recess (SSD) structure that embeds an epitaxial strained SiGe thin film that significantly improves hole mobility in the channel region. Scale down of critical dimensions (CD) in current and future CMOS devices puts ever increasing emphasis in reducing post-etch Si surface damage in a source-drain (SD) recess structures. For a typical SSD application, the roughness of Si surface obtained after SD etch governs both the epitaxial growth of SiGe as well as the roughness of the SiGe layer, and ultimately determines the device performance. This paper will discuss the factors that contribute to the Si surface roughness arising from a representative SD process etch step and its impact on the subsequent SiGe epitaxy and device performance. Typically, the SD etch sequence may consist of an anisotropic etch (halogen/oxygen based chemistry) followed by an isotropic etch (halogen/halogen based chemistry). Surface roughness of the etched silicon is quantified and spatially resolved through atomic force microscopy and surface haze measurements, and contributions of the anisotropic and isotropic etch steps to surface roughness are inferred. The effects of halogen ratio and relative halogen atom reactivity in the isotropic etch chemistry on surface roughness and the vertical-to-lateral (V/L) etch ratio in the SSD recess feature will be discussed and a surface reaction model proposed to characterize roughness evolution.

9:00am **PS-MoM3 Improving Etch Processes by using Pulsed Plasmas**, *M. Darnon*, *M. Haass, P. Bodart, G. Cunge, C. Petit-Etienne, M. Brihoum, R. Blanc*, CNRS-LTM, France, *T. David*, Cea Leti Minatec Campus, France, *E. Pargon, L. Vallier, O. Joubert*, CNRS-LTM, France, *S. Banna, T. Lill*, Applied Materials, Inc. **INVITED**
The etching processes for integrated circuits fabrication becomes extremely challenging when the devices dimensions are downscaling and the etch process has to stop on the ultra thin layers (less than 2nm) of materials. Perfect control of the passivation layers and mask erosion are required to precisely control the patterns profiles, which necessitates using flows and energies of plasma species in ranges which can not be attainable with current plasma technologies. In addition, limiting the plasma induced damage to thin layers requires very low ion energies which are not accessible in current plasma technologies. One promising solution is to pulse the plasma in conventional industrial reactors at very low duty cycle. Using this solution, the ratio of radicals and ions as well as their energy can be fine tuned in ranges that are unreachable otherwise, and very low energy

ions are produced which strongly minimizes the damage to the thin layers exposed to the plasma.

Experiments are performed on a 300mm diameter Inductively Coupled Plasma chamber commercialized by Applied Materials (DPSII G5) equipped with the pulsync system to enable plasma pulsing in an industrial reactor.

In this paper, we will show how plasma pulsing can be used to improve uniformity and pattern profiles by better controlling the passivation layer formed on the patterns sidewalls during the etching. In addition, we will demonstrate that the reduction of the average ion energy as well as the use of molecular ions decreases mask erosion, as well as damage to ultrathin etch stop layers. Morphological characterization, surface characterization and plasma diagnostics will be correlated to explain the mechanisms responsible for the process improvement.

9:40am **PS-MoM5 HfO₂ Etching by Pulsed BCl₃/Ar Plasma**, *P. Bodart*, *C. Petit-Etienne, G. Cunge, F. Boulard, M. Darnon, L. Vallier, E. Pargon*, CNRS-LTM, France, *S. Banna, T. Lill,* Applied Materials, Inc., *O. Joubert*, CNRS-LTM, France
Plasma etching of high-k materials, including HfO_2, has attracted much attention due to the necessity to integrate these materials in MOSFET transistor. After the metal gate patterning process, the high-k dielectric film must be removed from the source and drain regions of the transistor. It is today well established that HfO_2 can be etched selectively towards SiO_2 and Si in BCl_3/Cl_2 plasma. However, it remains difficult to minimize the plasma induced damages (Si amorphisation and recess) in the source/drain transistor regions in such processes. Since pulsed plasmas have shown a capability to minimize Si-recess in typical silicon gate oxide etching processes, we have investigated their potential for HfO_2 etching.

The experiments are performed in a 300mm DPS tool from Applied Materials. The chamber is modified to allow plasma diagnostic like UV-broad band absorption spectroscopy. The reactor is also connected to an Angle-Resolved X Ray Photoelectron Spectroscopy analyzer by a robotized vacuum chamber. The etching rate of HfO_2 sample (either 40 or 3.5nm-thick HfO_2 films with 8 Å SiO_2 interlayer deposited on Si substrates) and of SiO_2 samples (10 nm thick) are measured in real time by in situ multi-wavelength ellipsométrie.

We have evaluated the capability of pulsed plasmas to minimize the plasma induced damage of silicon during the etching of HfO_2 high-k gate dielectric. XPS analyses show that the perturbation of the bulk Si lattice is less pronounced with pulsed conditions, which is attributed to a lower ion bombarding energy. However, the formation of a BCl_x polymer selectively on the silicon (which is responsible for the HfO_2 to Si etching selectivity) is reduced when the plasma is pulsed leading to a loss of selectivity. VUV absorption spectroscopy indicates that the fragmentation of BCl_3 molecules, which leads to the formation of B-rich polymer precursors, decreases dramatically when the plasma is pulsed at low duty cycle. Therefore, as the duty cycle is reduced, the fluxes of B radicals to the wafer are reduced while the amount of Cl in the polymer increases. It follows that the polymer deposition rate drops, eventually leading to a loss of selectivity at the lowest duty cycles.

However, there are several ways to retrieve the process selectivity in pulsed plasma, such as reducing the BCl_3 flow in the gas mixture or working at higher pulsing frequencies (up to 10 kHz) to enhance B formation in the gas phase. Pulsing the plasma is not a magic knob since it strongly changes the range of allows news physics and chemistry ranges plasma parameters.

However, plasma pulsing reduces significantly the plasma induced damages after process optimization.

10:00am **PS-MoM6 Study of Metallic Interfaces Etching for High-K Metal Gate stacks in CMOS 28 nm Technology**, *F. Chave*, STMicroelectronics, France, *L. Vallier*, CNRS-LTM, France, *P. Gouraud, C. Vérove*, STMicroelectronics, France, *O. Joubert*, CNRS-LTM, France
In CMOS technology, the downscaling of the transistor gate dimension, driven by ITRS roadmap specifications for advanced technology, requires the introduction of new materials. Dry etching step of those new "High-K Metal Gate" (HKMG) stacks is critical for the electrical performances of the devices and needs very accurate process control to achieve correct profiles, with a good Critical Dimension control. Moreover, characterization tools are now dealing with thin materials thicknesses sometimes around the limit of one full atomic layer. In this work we focus on dry etching process of 28nm technology High-K Metal Gate stacks. Several issues, especially for Metal/Capping layer interfaces, are investigated to better understand and control physicochemical interactions.

Most of etching experiments are carried out in a 300mm DPS AdvantageEdge™ etch chamber from Applied Materials allowing in situ diagnostic, as reflectometry and spectroscopic ellipsometry. This modified tool permits to transfer wafer under vacuum to a customized Theta 300 XPS

system from Thermo Fisher Scientific for quasi in-situ analysis without exposure to the environment. Samples were 300mm diameter Si wafer with full sheet and/or patterned deposited layers. Industrial 28nm photolithography & plasma etching process developed to gate first approach were employed.

Preliminary experiments have shown that foot and undercut effects are possible profiles deformations due to metallic interfaces, and we have to control these deviations.

Consequently, we focused first on the TiN/LaO interfaces which we highlight as a critical step. TEM analyses demonstrate that LaO capping layer acts as etch stop layer for current TiN etching chemistries. Therefore, a specific step for LaO removal is needed; otherwise etching residues are left over.

Layer thickness and step time in the specific removal of Lanthanum oxide are some parameters which directly impact the under-layer materials with the observation of pitting on nMOS open areas or residues on pMOS.

XPS characterizations were carried out. Etching results analyses for TiN/LaO/TiN interface reveal the fact that after the whole stack etching step, some LaO residues remain on the sample surface although TiN disappear as evidenced from XPS survey scan. The conclusion is that TiN looks totally removed as Lanthanum can be redeposit or for certain push-forward. Such as mechanisms were considered, and experiments were carried out to understand and complete this result.

Integration of thin metallic and capping layers in gate stacks challenge dry etching process. Those results highlight the trend of interactions all across the plasma etch process.

11:00am PS-MoM9 Double Patterning Challenges for the sub 22nm CMOS Nodes, *S. Kanakasabapathy*, *R. Jung, M. Hartig, S. Schmitz, Y. Yin*, IBM Research, *S. Raghunathan, L. Jang,* GlobalFoundries, *E. McLellan, S. Burns, S. Holmes, C.S. Koay,* IBM Research, *R.H. Kim,* GlobalFoundries, *G. Landie,* ST Microelectronics, *D. Horak,* IBM Research, *Y. Mignot,* ST Microelectronics, *S. Seo, S.T. Chen, J. Arnold, M. Colburn, B. Haran,* IBM Research

Wavelength and Numerical Aperture scaling in optical lithography have allowed CMOS density scaling to march along the Moore 's Law curve for the past three decades. However, at the sub 22nm CMOS nodes, the print pitch faces a technological barrier at the 80nm mark for the Front, Middle and Back Ends of Line. Until further wavelength scaling becomes available through Extreme Ultraviolet (EUV), the industry's attention is focused on Double Patterning. Multiple Interdigitated Lithography and Sidewall Image Transfer (SIT) are the two broad categories of techniques under consideration. Interdigitated Lithography can be subdivided into approaches with and without multiple passes through etch. Both of these techniques present unique etch challenges in assembling looser pitch patterns into a composite mask and subsequent pattern transfer into the stacks of interest. We will review etch perspectives on the applicability of double patterning methods to various levels in the process flow.

In particular, Fins for FinFET technology represent the tightest pitch (approximately 40nm for the technology nodes in development at this time) and yield well to Sidewall Image Transfer. We will present the issues surrounding mandrel definition and spacer film properties for Fin definition. The Gate level poses competing requirements of overlay control between the simpler patterns and the need to attain multiple Critical Dimensions (CDs) and pitches. We will examine this and the challenges of etch into advanced gate stacks for the 14nm node. At the Interconnect levels, we will consider the challenges of transferring not only trenches but also self aligned via patterns at sub -40nm half pitch into ultra low-k (ULK) dielectrics.

11:20am PS-MoM10 Novel Etch Mechanism for High Selectivity Etching of Silicon Nitride over Silicon and Silicon Oxide for Spacer Applications, *S. Engelmann*, *J. Chang, E.A. Joseph, R.L. Bruce, N.C.M. Fuller, W.S. Graham, E.M. Sikorski, S. Balakrishnan, A. Banik, M. Gordon,* IBM T.J. Watson Research Center, *M. Nakamura, G. Matsuura,* ZEON Chemicals L.P., *H. Matsumoto, A. Itou,* Zeon Corporation

To continue scaling CMOS devices at the traditional pace following Moore's law, high selectivity of etch processes towards multiple materials is approaching nanoscopic dimensions. The spacer etch process is a very critical element in the CMOS device process flow as it ensures and enables the electrical isolation of source/drain and gate regions. Extremely high precision is needed to form a silicon nitride (SiN) spacer without damaging exposed Si, SiO_2, or other surfaces (SiGe or SiC for example). This process is even more challenging for non-planar devices (such as FinFETs and Trigates), where the plasma process needs to be able to form the spacer on the gate sidewall, but not the fin sidewall. At the same time the exposed SiO_2 and Si surfaces (if applicable) have to withstand the extended processing necessary to form the spacer.

Multiple etch gas chemistries have been evaluated and their impact on etch rates and selectivities for spacer applications have been evaluated. Surface analysis techniques such as XPS and FTIR have been applied in conjunction with OES analysis of the plasma to study the etch mechanisms leading to the observed etch rates. Fundamental differences in etch mechanism were found for different etch gas chemistries.

We observed that during conventional spacer processes, very little difference in plasma polymer deposition onto the respective substrates could be noted. A successful SiN spacer process was rather facilitated by a Si etch process that was selective to SiO_2, where excess oxidation lead to a conversion of Si to SiO_2. This also means that the etch rates of the SiN are limited by the simultaneous oxidation of the same. A potential solution to overcome this limitation would be to control the etch rate by polymer thickness, similar to high selectivity SiO_2 etching. An evaluation of this approach has yielded similar results as the general etch mechanism proposed by Schaepkens et al.[1] [#_ftn1] A novel etch chemistry was also evaluated that enables a different etch mechanism that cannot be described by the general model. The impact of the described mechanisms on actual CMOS devices will be discussed in detail.

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[1] [#_ftnref1] M. Schaepkens et al., J. Vac. Sci. Technol. A 17, 26 (1999)

11:40am PS-MoM11 High-Aspect Silicon Trench Oxidation in Downstream of Surface-wave Oxygen Plasma, *Y. Taniuchi*, **H. Shindo**, Tokai University, Japan

A low temperature and low damage silicon oxidation technique is highly required in various technology fields, such as in ULSI insulation layer formations, MEMS (Micro-Electro-Mechanical System) processes and other material surface treatments. In particular, in ULSI, the shallow trench isolation (STI) technique is inevitable to realize further integrations. In this process, so-called, a liner oxidation, in which the trench bottom is directly oxidized, becomes more severe, as the trench aspect ratio is further increased with the integrations. In MEMS (Micro-Electro-Mechanical System) processes, on the other hand, deep silicon trench etching with high aspect ratios is one of key technologies, and to realize a deep trench etching with a good directionality, a side wall passivation by the trench oxidation is inevitable. In this work, a silicon trench oxidation is investigated by employing a microwave oxygen plasma downstream under the condition of radio-frequency bias as well as the DC. In particular, the radio-frequency bias and the DC are superimposed and applied onto the substrate with the trench structure, and the oxidation rates at various portions of trench with the aspect ratio of 2 to 6 are examined as a function of the superimposed substrate bias. The oxidation depth shows a maximum in a very downstream of further position from the microwave window, indicating that the oxidation is due to negative oxygen ions. The silicon trench oxidation mapping, in which the oxidation film thickness is two-dimensionally plotted for the radio frequency bias and DC bias voltages, clearly demonstrates that the maximum is brought about along the line of the substrate bias of +20 V just above the plasma potential. In particular, the silicon trench bottom oxidation is just limited onto the higher radio frequency bias within the above condition. As for the dependence on the trench aspect ratio R, the oxidation at the trench bottom was attained 100 % of the trench top up to R=3, while at the trench bottom with R more than 4 it was only 60 %. The oxidation at the bottom of deep trench with the aspect ratio R= 6 was improved at the higher radio frequency bias. It is concluded that the oxidation is due to the negative oxygen ions in downstream.

Monday Afternoon, October 31, 2011

Marine Biofouling Focus Topic
Room: 105 - Session MB+BI+PS-MoA

Marine Antifouling Coatings
Moderator: A. Rosenhahn, Karlsruhe Institute of Technology, Germany

2:00pm MB+BI+PS-MoA1 Advances in Sustainable Technologies for the Prevention of Marine Biofouling, *R. Deshmukh,* University of Texas at Arlington*, P. Sheth,* University of North Texas Health Science Center*, R.B. Timmons,* University of Texas at Arlington*, J.A. Schetz*, University of North Texas Health Science Center **INVITED**
The cost associated with preventing the attachment of marine organisms to underwater surfaces (biofouling) is billions of dollars annually impacting numerous sectors including shipping, aquaculture, offshore drilling, and offshore tidal and wind power. Invariably the most effective biofouling control methods are ones that are biocidal in nature whereby a coating is impregnated with a toxin that leaches out over time. However, persistence and bioaccumulation of heavy metal-based and organic biocides, creates environmental and health problems that have resulted in their regulation. Vigorous hull cleaning, aimed at periodically removing biofouling organisms, disperses fine biocide-impregnated coating particles and this significantly increases biocide persistence in sediments where they are ingested by a variety of marine organisms and bioaccumulate.

Coatings that peel off under conditions of high shear, so called foul-release coatings, are another approach but such coatings are easily damaged, not amenable to grooming and ineffective against microfouling. Further, the most effective foul-release coatings are silicon-based and it is becoming increasing apparent that leaching of toxic silicon oils from the coating matrix plays a role in their superior antifouling performance. Other approaches have been to develop durable coatings with little antifouling activity but that can withstand repeated intense grooming. One of our long term objectives is to identify coating materials with surface properties discouraging the settlement of biofouling organisms but also durable enough to withstand cleaning.

Here we report on the discovery of a transparent, conformal, pin-hole free, and plasma-polymerizable polymer coating made from an inexpensive monomer material that drastically reduces (>90%) algae (*Ulva*) sporeling settlement and biomass accumulation without any observable toxicity towards *Ulva* or a non-target brine shrimp species (*Artemia*). Further the unpolymerized monomer has no antifouling effect indicating that potential leaching of monomer from coated surfaces does not account for the observed antifouling activity. Rather the antifouling effect is believed to rely on the presence of a specific chemical moiety because chemical modification of that moiety abolishes antifouling activity. Testing of other marine antifouling species such as microfouling bacteria (*Cellulophaga*) and macrofouling mussels (*Ischadium*) suggests that the antifouling properties of the polymer surface are selective for algae. Potential unique applications for this technology include the coating of algae bioreactor walls or light fixtures allowing for maximal illumination and easy cleaning.

3:00pm MB+BI+PS-MoA4 Development of a Comparative Protocol for Anti-Fouling Surfaces Based on Polymer Brushes, *A. Serrano, S. Zürcher, S. Tosatti,* SuSoS AG, Switzerland*, N.D. Spencer*, ETH Zurich, Switzerland
Marine surfaces are known to accumulate fouling material through the starting point of adhesion and settlement of proteins and cells. This effect can be manipulated through the modification and control of the substrate properties via surface functionalization. This approach has led to successful anti-fouling coatings based on biocidal agents containing copper or zinc compounds[1,2]. The environmental toxicity of these latter materials, however, has increased the demand for less adverse coatings. The use of ultra-thin films consisting of polymer brushes has been considered a promising alternative and many studies have been published in this field[3,4]. None, however, has focused on developing a protocol that allows a reliable comparison between the efficiency of different well-known anti-fouling polymers. This is one of the aims of this work and has been achieved by using a common, azide-terminated monolayer to which different non-fouling polymers, such as PEG, PEOXA, PVP and PVA, have been covalently bound. The different materials were compared by characterizing the structure-property relationship of the formed polymeric brushes. Also investigated was the role of the solvent used in the anti-fouling polymer solution as a key element to better control the surface homogeneity. A thorough analysis of the influence of this parameter on the conformation of the final polymer brush was based on ellipsometry, XPS and imaging ToF-

SIMS. Finally, the anti-fouling surfaces were subjected to a comparative biological study by exposure to complex proteins solution and *Ulva* zoospores, in order to validate the developed protocol.

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3:40pm MB+BI+PS-MoA6 Surface Modification of Polymers via Self-Stratification: Decoupling of Bulk and Surface Properties, *D.C. Webster*, North Dakota State University **INVITED**
Since materials interact with their surroundings via their surfaces, controlling the surface properties of a material are of critical importance. For materials to be used to mitigate biofouling, having the correct surface properties means the difference between a useful material and one that is unsuitable for the application. In many cases, the material properties of compositions which yield useful surface properties are not suitable for the bulk properties of the material. Thus, being able to decouple the surface and bulk properties is of interest in many areas.

Combining polydimethysiloxane (PDMS) with other polymer systems generally results in materials covered with PDMS due to its low surface energy and incompatibility with other polymers. However, if the PDMS is not chemically bound into the system, it can be easily removed from the surface. Thus, forming a copolymer of the PDMS with the other polymer is required for a durable system. Since polyurethanes are known as tough polymers due to extensive internal hydrogen bonding, combining PDMS with a polyurethane could lead to a material which is tough, but has a low surface energy surface provided by the PDMS. Thus, we have found that incorporating a reactive PDMS into a crosslinked polyurethane system can result in a material which has a low surface energy which is stable when immersed in water. High throughput screening has been used to aid in the identification and optimization of PDMS molecular weight, composition of end groups, and the amount of PDMS in the coating. A unique coating was also identified having discrete domains of PDMS on the surface. Coatings having good fouling-release properties have been prepared and tested in ocean immersion testing.

4:20pm MB+BI+PS-MoA8 Antifouling Behavior on the Surface of Polyelectrolyte Brushes in Water, *M. Kobayashi, M. Terada,* Jst, Erato, Japan*, A. Takahara*, IMCE, Kyushu University, Japan
Nature utilizes super-hydrophilic surfaces under wetted state by water to achieve oleophobicity and self-cleaning behavior. For example, fish can maintain a clean body surface by surrounding a thin layer of mucus containing calcium phosphate and protein, which protects oil attachment, marine fouling, and adhesion of marine organisms. In this study, high-density hydrophilic polymer brushes were prepared on Si-wafer by surface-initiated controlled radical polymerization of methacrylate monomers with ionic functional groups.[1] For example, poly(3-sulfopropyl methacrylate potassium salt) (PSPMK) and poly{2-(methacryloyloxy)ethyl phosphorylcholine} (PMPC) brushes with 50 - 100 nm thickness repelled both of air bubble and hexadecane droplet in water.[2] Even when the silicone oil was spread on the polyelectrolyte brush surfaces in air atmosphere, once the oil-sitting brush substrates were immersed in water, the oil quickly rolled up and detached from the brush surfaces due to the low adhesion force between the brush and oil caused by excellent affinity of polyelectrolyte brushes to water. Similar oil detachment behavior was observed on the hydrophilic poly(sodium methacrylic acid) (PMANa) and poly[3-{dimethyl(2'-methacryloyloxyethyl)ammonio} propanesulfonate (PMAPS) brushes,[3] whereas the oil still remained attached on the hydrophobic poly(2-perfluorooctylehtyl acrylate) (PFA-C8) brush even though the PFA-C8 brush shows relatively oleophobic property under air atmosphere. These hydrophilic brush surfaces would contribute to the excellent self-cleaning, antifogging, and antifouling properties without any surfactants

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4:40pm MB+BI+PS-MoA9 Non-fouling Polymer Chemical Gradients for the Investigation of Marine Bioadhesion, *O. Sterner*, ETH Zurich, Switzerland, *S. Zürcher*, SuSoS AG and ETH Zurch, Switzerland, *S. Tosatti*, SuSoS AG and ETH Zurich, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland

The accumulation of marine organisms on submerged man-made structures (referred to as marine biofouling) has great economical and environmental impact [1]. Numerous strategies to prevent or lower the extent of marine biofouling have been developed, ranging from biocidal coatings to coatings that either prevent adhesion, lower the strength of adhesion or combinations thereof [2-4]. Surface gradients offer a high-throughput approach to investigate the potency of such coatings, and have the additional advantage of reducing the error in experiments by replacing a set of single samples, including positive and negative controls, with a single substrate [5]. In this project, polymeric ultrathin coatings have been prepared using a versatile surface functionalization system based on a self-assembled monolayer of poly(allyl amine) grafted with photo sensitive perfluorophenyl azide functional groups. Gradients have been prepared using a straightforward approach to control the extent of azide to nitrene conversion over the surface, forming a polymer density gradient. Gradients of poly(ethylene glycol), poly(2-ethoxy-2-oxazoline) and poly(vinyl pyrrolidone) have been prepared and investigated for non-fouling action against zoospores from green macrofouling algae *Ulva* and two strains of marine bacteria. The gradients reveal a drastic reduction in bacterial adhesion at low polymer densities for all polymers investigated. Gradients have been characterised with variable angle spectroscopic ellipsometry (VASE) and the properties of the polymer coatings have been evaluated with time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and XPS.

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5:00pm MB+BI+PS-MoA10 Development of Poly(silyl urethanes) with Tethered Quaternary Ammonium Biocides as Antifouling Marine Coatings, *P.N. Coneski*, N.K. Weise, J.H. Wynne, Naval Research Laboratory

Due to the significant economic burden posed by high operational and maintenance costs of biofouled ships, the design of environmentally benign, antifouling marine coatings has been a significant interest for many researchers since the ban on traditional coatings was enacted. Current approaches for developing new marine coating materials have primarily focused on the preparation of low surface energy materials, such as modified polydimethylsiloxane (PDMS) and fluorinated polymers. These materials have shown great promise for reducing the adhesion strength of various fouling organisms, thus allowing hydrodynamic forces to release the foulants as the ship moves through water. Unfortunately, no existing material has been shown to eliminate adhesion of all of the numerous different fouling organisms, including zoospores, microalgae and diatomaceous species. As such, the development of marine coatings with multiple mechanisms of fouling prevention may be an important avenue of antifouling materials research. Poly(silyl urethanes) coatings have been developed via the reaction of various quaternary ammonium modified orthosilicates with polyisocyantes. Material properties including glass transition temperature, surface energy, and thermal stability have been investigated as a function of orthosilicate and polyisocyanate composition as well the inclusion or omission of low surface energy soft segments. The low surface energy of these materials should provide excellent fouling release properties, as has been seen with other PDMS-like materials, while the inclusion of bound quaternary ammonium biocides should further reduce the adhesion and propagation of fouling organisms at the material interface. Finally, the hydrolysable silyl ether crosslinking may prove to enhance the antifouling capabilities of these materials by allowing any fouled portions of the coating to slough away over time, generating a new active biocidal interface.

5:20pm MB+BI+PS-MoA11 A Preliminary Study on Porous Pt-TiO₂/Ti Electrodes with Electrochemically Microbubble-Induced Superhydrophobic Surfaces for Drag Reduction and Antifouling, *K.R. Wu*, *C.H. Hung, C.W. Yeh, J.C. Sun, J.K. Wu*, National Kaohsiung Marine University, Taiwan, Republic of China

We investigate a novel device that features a reduction in frictional resistance and antifouling hull surface of seagoing ships which are activated electrochemically by a series of porous $Pt-TiO_2/Ti$ electrodes. This device includes of a series of anodic and cathodic porous $Pt-TiO$ /Ti electrodes insulatedly mounted on the hull surfaces of which are electrically connected to a direct current (DC) power supply. The above-mentioned porous $Pt-TiO_2/Ti$ electrodes are fabricated by two steps; porous TiO_2/Ti plates are firstly prepared on pure titanium plates via a micro-arc oxidation technique and Pt nanoparticles are thereafter deposited on the porous TiO_2/Ti samples using magnetron sputtering. The DC power supply provides an adequate DC bias to the $Pt-TiO_2/Ti$ electrodes where hydrogen and oxygen microbubbles are electrochemically nucleated and formed herein in seawater. As a result, the microbubble-induced superhydrophobic surfaces are created and the reduction in frictional resistance and antifouling hull surface are obtained. Our preliminary tests reveal that no attachment organisms are found on the $Pt-TiO_2/Ti$ electrodes after 15 days of field seawater tests at an applied potential of 1.2 V and an energy consumed rate of about 4 W/m^2. On the other hand, organisms, mainly Crassostrea gigas and barnacles, attached and grew on the $Pt-TiO_2/Ti$ electrode that was not applied a DC potential. That is to say that attachment of organisms can be prevented. Furthermore, the $Pt-TiO_2/Ti$ electrodes yields a gas production rate of 800 cm^3/min m^2 by electrolysis of seawater at an energy consumed rate of about 18 W/m^2. Hence, the microbubble-induced superhydrophobic surfaces can be realized with this gas production rate for drag reduction of the ship hull.

Plasma Science and Technology Division
Room: 202 - Session PS+BI-MoA

Multiphase (Liquid, Solid, Gas) and Biological Related Plasmas
Moderator: A.M. Coclite, Massachusetts Institute of Technology

2:00pm PS+BI-MoA1 Atmospheric-Pressure Microplasmas for Novel Electrochemical Applications, *S.W. Lee*, *R.M. Sankaran*, Case Western Reserve University

Plasmas formed at sub-millimeter spatial scales operate stably and close to non-thermally at atmospheric pressure and are a source of ions, electrons, and other electronically excited states at ambient conditions. Overall, these features make microplasmas suitable for novel electrochemical applications where gas-phase species (e.g electrons) in the plasma can directly interact with ionic aqueous electrolytes to initiate redox reactions.

In this talk, we will present two approaches to microplasma-based electrochemistry that we have developed for nanoparticle synthesis. In one approach, microplasmas are formed at the surface of a liquid electrolyte and operated similar to an electrochemical cell with the plasma as the cathode and a solid metal immersed in the electrolyte as the anode [1]. Metal cations in solution such as Ag+ are electrochemically reduced by the plasma to solid metal, resulting in the formation of metal nanoparticles without any chemical reducing agent. Alternatively, thin films of metal cations dispersed on a polymer are electrochemically reduced by a rastered microplasma [2]. This configuration allows microscale patterns of metal nanoparticles to be produced without the need for lithography. Recently, we have extended our patterning method to the reduction of metallopolymers which are novel molecular structures that can be used as a template for metal ion and metal particle formation [3]. This strategy has enabled patterns of metal nanoparticles to be prepared which are beyond lithographic limits. We will discuss our experimental techniques in detail, as well as the properties of the nanoparticles as assessed by UV-Visible absorbance spectroscopy, X-ray diffraction, and transmission electron microscopy.

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2:20pm PS+BI-MoA2 Water Containing Non-Equilibrium Atmospheric Pressure Plasmas, *P.J. Bruggeman*, Eindhoven University of Technology, the Netherlands **INVITED**

During the last decade water containing non-equilibrium atmospheric pressure plasmas have received a continuously increasing attention in view of their potential in biomedical, environmental, chemical synthesis and material processing applications. This evolution coincides with a strong need for improved diagnostics to enable us to unravel the complex physics and chemistry of water containing plasmas. Both discharges containing a liquid water phase and only water in the vapor phase will be addressed in this contribution.

We will give an overview of the physical and chemical properties of these discharges. The main plasma parameters such as the electron density, gas and electron temperature will be presented and the complications of the interpretation of the diagnostics to obtain these plasma parameters will be discussed. Water containing discharges produce high radical densities such as OH, which is a key radical in several applications. Due to the often high electron density of these discharges recombination reactions are very important not only for radical production but also to explain the optical emission of these discharges. Key differences between liquid water containing discharges and more conventional gas discharges will be discussed.

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3:00pm PS+BI-MoA4 Mechanism of Au Nanoparticles Formation in Solution Plasma, *M.A. Bratescu, O. Takai, N. Saito*, Nagoya University, Japan

The Solution Plasma Processing (SPP) has been developed in our laboratory to synthesize nanoparticles and to improve surface properties of carbon nanomaterials by decorating with different nanoparticles or binding functional groups on the surface. The purpose of the present study is to investigate the mechanism of the Au nanoparticles (NP) formation in the SPP and to correlate the SPP properties with the Au NPs characteristics (morphology, size and surface functionalization). The investigation was conducted by changing the solution pH, using the same surfactant and keeping the same processing parameters.

The Au NPs were synthesis in an aqueous solution of 1 mM HAuCl$_4$·3H$_2$O used as precursor, 1 mM hexadecyltrimethylammonium chloride (CTAC) used as surfactant, and NaOH used to adjust the solution pH (3.2, 6.5 and 11.2). The plasma was produced by using a pulsed high voltage (HV) power supply with the peak voltage and current of 2 kV and 1 A, respectively and the pulse width of about 1 μs. Plasma was characterized by optical emission spectroscopy (OES). The OES gives information about the presence of the relative number densities of the radicals as H, OH, O, and O$_2$ and from these data the electron temperature and density were evaluated.

On surface, in high vacuum environment, the Au NPs were characterized by Transmission Electron Microscopy (TEM), Secondary Ion Mass Spectrometry Time of Flight (SIMS - ToF) and X-rays Photoelectron Spectroscopy (XPS). In solution, as prepared, the Au NPs were characterized by UV-visible spectroscopy and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy.

The size of the synthesized Au NPs depends on the initial pH of the solution. In a low pH solution, the particle size was around 15 – 20 nm diameter and in a solution with a higher pH value than 6, the NPs diameter was found to be 2 – 5 nm. The negative SIMS-ToF measurements reveals the presence of the Au$^-$, AuCl$^-$ and AuN$^-$ ions in the solution with a pH 3 and AuO$^-$ in a solution with pH 11. In a solution before plasma processing, with a low pH value the negative ions Au$_2$Cl$^-$ and Au$_3$Cl$_2^-$ were detected, which can suggest an initial agglomeration of Au atoms in solution. The binding functional groups on the Au NPs are confirmed by the XPS analysis.

The correlation among information of the Au NPs morphology, the binding atoms on Au surface, plasma electron temperature and density and the

formation of the Au complexes, during the Au NPs synthesis will be presented and discussed.

3:40pm PS+BI-MoA6 Pulsed Plasma Studies of 2-chloro-p-xylene, *I.C. Estrada-Raygoza, G. Padron-Wells, P.L.S. Thamban, L.J. Overzet, M.J. Goeckner*, University of Texas at Dallas

Chemical vapor deposited parylene-C is widely used for applications ranging from biomedicine to microelectronics. In our work, we use 2-chloro-p-xylene (2ClpX) as a precursor to deposit plasma polymerized Parylene C. Here we report data aimed at determining the dissociacion mechanisms of the 2ClpX in the plasma. Specifically that data is from: in situ Fourier transform infrared spectroscopy (FTIR); plasma optical emission spectroscopy (OES); and electron beam OES. The main dissociation products are HCl, methane and acetylene. We also observe atomic and molecular hydrogen and chlorine, HCl ion, CH and the characteristic broad aromatic band in the 300 nm region. Both frequency and duty cycle have a strong effect in 2ClpX dissociation. When the pulse period is smaller than the diffusion time, the discharge behaves as continuos wave system, independent of the duty cycle used. When the pulse period is much larger than the diffusion time, the discharge behaves different and very little break up of the monomer is detected. When the pulse period is similar to the diffusion time, then the effect of duty cycle is considerable. This work is supported in part by NSF (Grant CBET- 0922962), Verity Instruments and CONACYT Grant 170201.

4:00pm PS+BI-MoA7 Deactivation of Lipopolysaccharide and Lipid A by Ar/H$_2$ Inductively Coupled Plasma, *E. Bartis,* University of Maryland, College Park, *T.-Y. Chung, N. Ning, J.-W. Chu, D.B. Graves,* University of California, Berkeley, *J. Seog, G.S. Oehrlein,* University of Maryland, College Park

Low temperature plasma (LTP) treatment of surfaces is a promising path toward sterilization of bacteria [1]. Past works have shown plasma-induced degradation of bacteria [2], but little knowledge exists regarding the plasma-induced chemical modifications in biomolecules that result in inactivation since various plasma species, e.g. ions, reactive radicals, and UV/VUV photons may aid in inactivation. Lipopolysaccharides (LPS) are a main component of the outer membrane of gram-negative bacteria and are difficult to remove from surfaces by conventional methods [3]. LPS is made up of a polysaccharide chain and lipid A and lipid A elicits an immune response in animals [1]. Previous studies have found that adding H2to an Ar plasma leads to a reduction of infrared bands originating from the aliphatic chains of lipid A, namely C-Hx stretching, C-O, and amide bands [4]. This study aims to distinguish the roles of physical sputtering, chemical attack by H-atoms, and plasma-generated VUV. LPS-coated silicon chips were exposed to LTP (Ar, H2, and Ar/H2 mixtures) to explore the effects of plasma composition/ion energy on the etch rates (ER) and chemical and optical properties of LPS. Real-time in-situ ellipsometry was used to monitor ER and changes in the LPS film's optical density during plasma exposure. The real-time data showed that Ar plasmas create a dense film on the surface that decreases in density with H2addition. The films were etched fastest in Ar discharges mixed with ~10% H2and were slowest in pure H2. Since previous work [4] found that adding H2to an Ar discharge enhanced sterilization, these results may indicate that chemical modification rather than rapid erosion may be more important for inactivation. After LTP treatment, samples were characterized by vacuum-transfer to x-ray photoelectron spectroscopy (XPS) to measure the chemical modifications taking place in the LPS layer. With XPS, we measured a decrease in the intensity of the C-C/C-H peak, which indicates that the aliphatic chains in lipid A were removed. The N/C ratio increases approximately equally in all discharges, which suggests that gas chemistry does not have a large impact on amides. Complementary studies with Lipid A will be presented as well as results of a VUV optical filter approach used to probe VUV-induced LPS modifications in real time by in-situ ellipsometry while protecting the material against ion bombardment.

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4:20pm PS+BI-MoA8 Development of Plasma Treated Mn Induced Nano-arrayed Structures in Sol-gel Derived TiO$_2$ Matrix for Biosensing Applications, *R.R. Pandey,* Centre for Cellular and Molecular Biology, India, *K.K. Saini,* National Physical Laboratory, India, *M. Dhayal*, Centre for Cellular and Molecular Biology, India

We describe Mn doped TiO$_2$ nanomaterial-based biosensors modified by high pressure RF plasmas for biosensor applications which activates nanostructure matrix and greatly enhanced enzyme loading capacity for development of high sensitivity biosensors. As a test modal, effects of

plasma treatment on a novel potentiometric urea biosensor for selective and quantitative recognition of urea by immobilizing urease onto Ti/urease-imprinted Mn induced TiO_2 film has been studied and monitoring the potentiometric response caused by the immobilized urease/urea reaction system was carried out. These platforms has been characterized by XRD, XPS, FTIR, SEM, cyclic voltametry to determine the changes in structure, surface chemistry and electron transfer characteristics of platforms after plasma treatments and have been correlated with improved response of biosensor.

4:40pm **PS+BI-MoA9 Growth Promotion of Bread Yeast using Atmospheric Pressure Dielectric Barrier Discharges**, *S. Kitazaki*, *K. Koga, M. Shiratani,* Kyushu University, Japan, *N. Hayashi*, Saga University, Japan

Nonthermal atmospheric pressure plasmas have been employed for biomedical processing applications, because they provide high density radicals at a low gas temperature [1]. Recently, nonthermal atmospheric pressure plasmas as well as low pressure plasmas have been employed for growth promotion of plant cells [2,3]. In this study, we have developed a scalable atmospheric dielectric barrier discharge (DBD) device for biomedical processing in a large area and have applied the device to growth promotion of bread yeast. The device consisted of 20 electrodes of a stainless rod of 1 mm in outer diameter and 60 mm in length covered with a ceramic tube of 2 mm in outer diameter. The electrodes were arranged parallel with each other at a distance of 0.2 mm. The dry yeast was set at 1 mm under the electrodes. The discharge voltage and frequency were 10 kV and 10 kHz, respectively. The plasma treatment was carried out in the air. The treatment duration T_{on} was 50, 100 and 150 s. After the treatment, yeast was suspended in 0.5 ml yeast extract peptone dextrose (YPD) medium and agitated with a vortex mixer. 1 μl of sample was mixed with 99 μl YPD medium in a micro well plate and cultivated using a shaking incubator at 30 °C. To obtain growth curve of yeasts time evolution of 660 nm light absorbance of the samples was measured with a micro plate reader. For the control, the absorbance is almost constant until t = 15 hrs after the beginning of the cultivation, which corresponds to the lag phase, and then it exponentially increases with t, the exponential growth phase. For yeast with the plasma treatment, the absorbance increases from t = 0 hrs. At t = 10 hrs, the maximum absorbance for T_{on} = 150 s is 6.6 times as high as that for the control. From t = 10 to 15 hrs, the gradient of the absorbance becomes gradual. After t = 15 hrs, the absorbance increases exponentially with t. The plasma treatment reduces the lag phase of yeast growth and enhances the growth rate. The growth promotion tends to be enhanced with increasing T_{on} from 50 to 150 s. The growth promotion, therefore, depends on the dose of radicals produced by discharge plasmas.

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5:00pm **PS+BI-MoA10 Plasma Deactivation of Pyrogenic Biomolecules: Vacuum Ultraviolet Photon and Radical Beam Effects on Lipid A**, *T.-Y. Chung**, *N. Ning, J.-W. Chu, D.B. Graves,* University of California, Berkeley, *E. Bartis, J. Seog, G.S. Oehrlein*, University of Maryland, College Park

Conventional medical instrument sterilization methods are generally ineffective in completely removing harmful biological residues [1]. Biomolecules such as proteins and other pyrogens from bacterial residues are particularly resistant to elevated temperature and are not easily removed by conventional procedures [2, 3]. For example, the presence of lipopolysaccharide (LPS) in host tissue or blood circulation could lead to a generalized sepsis syndrome including fever, hypotension, and respiratory dysfunction and may lead to multiple organ failure and death [4]. Low temperature plasma is a promising technique for sterilization/deactivation of surgical instruments or medical devices, but its effectiveness against such targets is incompletely understood [5]. In this study using a vacuum beam system, we chose lipid A, the major immune-stimulating region of LPS, as a model biomolecule to study. Lipid A consists of a β-1,6-linked D-glucosamine (GlcN) disaccharide carrying two phosphoryl groups. This structure is attached to multiple acyl chains by ester or amide linkage [6]. After vacuum ultraviolet (VUV) photon exposure, loss of CH_2/CH_3, C=O ester, and P=O absorption peaks were observed by ex-situ transmission Fourier transform infrared (FTIR) spectroscopy, but the C=O amide absorption peak was only mildly affected. Monitoring photolysis products from lipid A films by in-situ mass spectrometry, we observed cracking

patterns similar to those of alkanes/alkenes with a carbon number ~11-13. This result suggests that VUV photons remove phosphate groups and break ester linkages leading to desorption of acyl chains. Endotoxicity of lipid A is known to be primarily determined by the number and length of acyl chains as well as the phosphorylation state and the disaccharide backbone [6]. The present results therefore indicate that plasma-generated VUV reduces the endotoxicity of lipid A, in support of the hypothesis of Rossi et al. [7]. We report the effects of VUV and radical (H, O) exposures on endotoxicity based upon chemical structural change in Lipid A. Synergism of various beams is compared with plasma exposures and corresponding molecular dynamic (MD) simulations.

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[3] L. Moesby et al., Eur. J. Pharm. Sci. **26**, 318 (2005)

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[6] C. Erridge, E. Bennett-Guerrero, and I. R. Poxton, Microbes Infect. **4**, 837 (2002)

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5:20pm **PS+BI-MoA11 Charge Transfer Reactions at the Plasma-Liquid Interface**, *M. Witzke*, *C. Richmonds, B. Bartling, S.W. Lee, J. Wainright, C.-C. Liu, R.M. Sankaran*, Case Western Reserve University

Electrochemical reactions are normally studied at the interface of a solid metal electrode and an aqueous ionic electrolyte. A smaller number of experiments exist, dating back to more than 100 years ago[1], of plasmas formed at the surface or inside of liquids to initiate electrochemical reactions at the interface of a plasma electrode and a liquid electrolyte. Despite this long history, reactions at the plasma-liquid interface remain poorly understood. Plasmas that are formed at low pressures require liquids with extremely low vapor pressure, limiting previous studies to ionic liquids (i.e. molten salts)[2]. In addition, plasmas are characterized by a complex environment (e.g. ions, electrons, UV, etc.) which has made it difficult to differentiate charge-transfer reactions from other non-faradaic reactions such as radical generation and chemical dissociation.

We have recently developed a novel microplasma source that allows a non-thermal, atmospheric-pressure plasma to be stably formed at the surface of aqueous ionic electrolytes[3-5], facilitating fundamental study of charge-transfer reactions at the plasma-liquid interface. Electron transfer reactions between the plasma and the liquid are studied by using the well-known ferricyanide-ferrocyanide redox couple. The electrochemical reduction of ferricyanide is monitored by UV-vis absorbance spectroscopy and cyclic voltammetry. We find that ferricyanide is indeed reduced by the plasma, confirming that charge transfer reactions can occur at the plasma-liquid interface. The rate of ferricyanide reduction is found to depend on the discharge current, which controls the electron flux delivered to the surface of the solution. By comparing the (discharge) current to the amount of ferricyanide reduced, we obtain a reduction efficiency of ~1%. To address the relatively low efficiency, we have measured the potential at the plasma-liquid interface to determine whether the potential is high enough for water electrolysis and measured hydrogen generation by mass spectrometry. In this talk, we will present our overall methodology and discuss these results in detail.

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2. S. Z. El Abedin, M. Polleth, S. A. Meiss, J. Janek, and F. Endres, *Green Chemistry* **9**, 549 (2007).

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* Coburn & Winters Student Award Finalist

Plasma Science and Technology Division
Room: 201 - Session PS+SE-MoA

Advanced FEOL / Gate Etching II

Moderator: A. Kadavanich, Mattson Technology

2:00pm **PS+SE-MoA1 Mechanical Analysis of the Line Edge Roughness in the sub-20nm Line Patterns**, *S.W. Park*, *K.H. Baek*, Samsung Electronics Co., Ltd, Republic of Korea, *S.H. Choi, J.S. Hong*, Lam Research Corporation, *K.S. Shin, Y.G. Shin, H.G. Kang*, Samsung Electronics Co., Ltd, Republic of Korea

In this study, the deterioration of line edge roughness during plasma etching process was analyzed to find possible control parameters. According to the aggressive design rule shrinkage of memory devices, the physical width of line patterns has become around 20nm. Controlling line edge and width roughness now became one of the biggest challenges in patterning process. Though a number of studies on this matter have done, the wiggling of line patterns is still making the migration slower. It is well know truth that the line edge and width roughness are mainly caused by the projection of poor photoresist patterns. However, the recent line patterns of around 20nm design rules experience severe wiggling added from the plasma etching process. This study focused on this etch-induced deformation that increased line edge roughness from the prior status. The final line edge roughness was assumed as the sum of the wiggling projected from that of mask pattern and the deformation during plasma process. The deformation part was explained with the equations of the mechanical beam theory assuming several stress sources originated from the plasma. This newly introduced approach could suggest the direction of process modification for more robust profile against deformation. Moreover, combining with the material properties of commonly used materials, this approach could estimate the extent of lateral deformation so that the ultimate size of line patterns could be expected in the aspect of line edge roughness.

2:20pm **PS+SE-MoA2 Dependence of ArF Photoresist Polymer Structure on Line-Edge-Roughness Formation during Plasma Etching Processes**, *T. Uesugi*, *A. Wada*, Tohoku University, Japan, *S. Maeda, K. Kato, A. Yasuda, S. Sakuma*, Mitsubishi Rayon, Japan, *S. Samukawa*, Tohoku University, Japan

ArF excimer laser (193nm) lithography technique is widely used in the fabrication of sub-50-nm devices. During plasma etching processes, however, the activated species radiated from plasma, such as ions, radicals, and photons, cause damages to ArF photoresist, resulting in low etching resistance and formation of line-edge roughness (LER). To solve these issues, we investigated the interaction between irradiated species from plasma and polymer structure of ArF photoresist. In our previous study, we found that improvement of stability of lactone group in side chain of ArF photoresist realized decrease in etching rate and reduction of the surface roughness of ArF photoresist.

In this study, to further improve the etching resistance and the surface roughness of ArF photoresist, we proposed a new polymer structure of ArF photoresist. Our newly developed ArF photoresist structure has acrylate group in main chain polymer structure, while usual ArF photoresist has methacrylate group in main chain polymer structure. We prepared silicon wafers coated by ArF photoresists with methacrylate group and acrylate group and etched them using chlorine plasma. As a result, these two types of photoresists had almost same etching rates. This result suggests that main chain structure of ArF photoresist does not affect its etching rate. On the other hands, the surface roughness of acrylate type photoresist after etching was drastically reduced in comparison with that of methacrylate type photoresist. It is considered to be due to stronger bonding energy of acrylate group than methacrylate group. From this result, it is concluded that the acrylate type ArF photoresist structure is very effective to suppress the roughness formation in ArF photoresist.

2:40pm **PS+SE-MoA3 193nm Photoresist Pre-Treatments Before Plasma Transfer to Improve LWR Transfer and CD Control**, *E. Pargon*, CNRS-LTM, France, *L. Azarnouche*, ST Microelectronics, France, *M. Fouchier, K. Menguelti, O. Joubert*, CNRS-LTM, France

Linewidth roughness (LWR) is today one of the main parameters that limits our ability to shrink the transistor gate dimension down to 20nm. Indeed, LWR needs to be controlled down to 2nm to ensure good electrical performance of the future CMOS device, while state of the art patterning techniques only allows 4-3 nm gate LWR at best. The major issue in decreasing the gate LWR comes from the fact that the significant LWR of the resist pattern printed after 193nm lithography (about 6nm measured by CDAFM) is transferred into the gate stack materials during the subsequent plasma etching processes. One way to minimize the final gate LWR is to apply various pre-treatments to the resist patterns obtained right after lithography (before any plasma pattern transfer step).

In the present study, we have used CD-SEM and CD-AFM techniques to investigate the impact of different types of resist pre-treatments (combining plasma exposure (HBr, Ar, H_2 plasmas), vacuum ultra violet (VUV) light exposure, and annealing) on the photoresist LWR and profile. Many characterization techniques (FTIR and Raman spectrometries, ellipsometry, chromatography, DMA, TGA) have also been used to characterize the physico-chemical modifications of photoresist films responsible for the resist smoothening. We have also investigated the benefits of those resist pre-treatments on both LWR and CD control after pattern transfer in different stacks of materials.

We will show that all treatments generate resist chemical modifications that lead to a decrease in resist LWR while the etch resistance is not always improved. All treatments have in common the cleavage of the side groups (lactone group for plasma treatment and protecting group for annealing treatment) and a decrease of the glass transition temperature that seems to have a direct impact on the LWR decrease. But some other mechanisms compete according to the treatment used and its duration: main chain scission and crosslinking, leading to some different etch resistance improvement. Consequently even if some specific treatments (VUV light exposure, annealing) can improve the resist LWR before transfer, the subsequent plasma etching steps can degrade it and also induce a loss of CD control. We will show that by combining plasma exposure and annealing treatment the photoresist LWR could be decreased down to 2.6nm and that this LWR could be transferred into polysilicon gate without LWR and CD degradation.

3:00pm **PS+SE-MoA4 Plasma Smoothing of Extreme Ultraviolet Photoresist: LWR Reduction at 30nm Half Pitch**, *E. Altamirano-Sanchez*, *A. Pret Vaglio, R. Gronheid, D. Marc, W. Boullart*, IMEC, Belgium

Over the past years a tremendous amount of effort has been put on Extreme Ultraviolet lithography (EUVL) for printing the 16nm node. In 2010 imec's EUV alpha demo tool printed for the first time a 16nm node SRAM cell using state-of-the-art EUV photoresist (PR). In order to meet the line width roughness (LWR) requirements for the 16nm node, we have investigated plasma smoothing techniques on 30nm half pitch lines after exposure.

In this contribution we will report our findings on EUV PR plasma treatment (PT) using H2, Ar and HBr for LWR reduction; and subsequent, in-situ PR encapsulation for preserving the improved LWR during subsequent pattern transfer. Currently we are investigating the vacuum UV role during the H2 PT using MgF2 windows. In parallel, we are characterizing a PR resist encapsulation carried out in-situ (in the etching chamber). The encapsulating layer is characterized through various analytical techniques, such as: XPS, Ellipsometry, mass metrology and TEM. These characterizations will provide understanding of how the H2 plasma improves the LWR and of how the PR encapsulation preserves the PR pattern allowing a straight HM patterning profile.

This study was carried out on 300 mm silicon wafers with the following patterning stack, from top to bottom: 50 nm PR/20 nm under layer (UL)/15 nm SiOC/40 nm amorphous carbon layer (ACL). The dry etching was carried out in a ICP like reactor from Lam research (Kiyo C reactor TCPTM)

Power spectral density (PSD) analyses have shown that Ar and HBr plasmas do not improve the LWR of EUV PR as they do on 193i PR. Using the correct conditions in the ICP reactor, H2 plasmas can improve LWR by ~30% without CD bias; in other words no PR reflow was detected.

After the H2 plasma treatment, the pattern was transferred into the UL using a CH2F2/CF4/O2 gas mixture. This chemistry provides on the one hand a high PR passivation but on the other hand induces a PR pattern degradation, which is translated into higher LWR. A novel alternative for maintaining the improved LWR after H2 PT was to deposit in-situ (in the ICP reactor) a silicon containing layer that encapsulates the PR and preserves the improved LWR when the pattern is transferred into the UL, the SiOC and the ACL.

3:40pm PS+SE-MoA6 Controlling Line Edge Roughness for Aggressively Scaled CMOS Devices by Reducing Organic Underlayer Deformation, *H. Miyazoe*, S.U. Engelman, M. Glodde, M.A. Guillorn, M. Brink, A. Banik, W.S. Graham, E.M. Sikorski, N.C.M. Fuller, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, control over line edge roughness (LER) and line width roughness (LWR) is approaching atomic scale for the 14 nm node and beyond. When the line/space patterns are decreased, deformation of the organic underlayer material occurs during plasma processing, which adversely impacts pattern transfer into substrate material to fail. We previously reported that vacuum ultraviolet (VUV) "curing" (modification) of the organic under layer material by plasma discharges is a promising approach to extend the process window for obtaining high fidelity pattern structures [1]. To understand the details of this approach in more detail, we exposed VUV light at various wavelengths corresponding to the absorption energies of various underlayer materials by synchrotron radiation on "unopened" and "opened" samples comprising stacks inclusive of the underlayer material. We found that exposing underlayers to certain absorption maxima of the patterning material maximize the curing effect. Specifically, for the underlayer material trademarked as NFC, absorption maxima at 155 nm had relatively large effect, reducing LER by as much as 37%. Curing treatments on "unopened" (post lithography) samples comprising varying underlayer materials effectively reduced the pattern deformation, though much less effective than on previously "opened" samples comprising the same. Similarly, chemical and physical effects of the plasma on underlayer material deformation were investigated. To investigate the changes based on chemical modification by plasma, we have generally found that the non-selective pattern transfer plasmas are better than highly selective processes to minimize the deformation. In addition, we also noticed that the ion energy of the discharge plays an important role in the deformation and found that the extent of pattern deformation decreased for lower energies. In addition, many commercially available organic underlayer materials were tested with respect to their composition and hardness. We found that the relative hydrogen content of the underlayer material seemed to correlate with the deformation behavior, while little effect was seen for hardness. These initial findings show that a close interlock between patterning materials, lithography and plasma processes has to be executed to minimize effects such as LER for future technology nodes.

[1] N.C.M. Fuller *et al.*, AVS presentation (2007).

4:00pm PS+SE-MoA7 Single Digit Nano Plasma Etching, *D.L. Olynick*, Lawrence Berkeley National Laboratory **INVITED**

One of our themes at the Molecular Foundry at LBNL is "Single-Digit Nanofabrication" (SDN) which describes our efforts to pattern materials with resolution, precision, and control at the sub-10 nm scale. At this scale, we enable research and applications in areas such as nanoelectronics, nanomagnetics, nanofluidics and plasmonics. For instance, the Molecular Foundry's work on graphene nanomeshes using SDN show a band gap opening with sub-bands.[1] However, the patterning and plasma pattern transfer for SDN present significant challenges and the question arises, "What are the limits?"

In this talk, I will survey nanoscale etching work from 30-3 nm to demonstrate the challenges and opportunities for plasma nanopatterning. High resolution patterns are made using a variety of materials and techniques including atomic layer deposition, directed self-assembly and electron beam and nanoimprint lithographies. Recent work with cryogenic etching and simulation in the SDN regime will be highlighted.

1.Liang, X.; Jung, Y.-S.; Wu, S.; Ismach, A.; Olynick, D. L.; Cabrini, S.; Bokor, J., *Nano Lett* **2010** 10, pp 2454-2460.

This work was performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, and was supported in part by the U.S. Department of Energy under Contract No. DE-AC02—05CH11231

4:40pm PS+SE-MoA9 Ar and He Plasma Pretreatments of Organic Masking Materials for Performance Improvements during Plasma Pattern Transfer, *D. Metzler*, F. Weilnboeck, N. Kumar, G.S. Oehrlein, University of Maryland*, S. Engelmann, R.L. Bruce, N.C.M. Fuller*, IBM T.J. Watson Research Center

Plasma based pretreatments (curing) of organic masking materials have been shown to offer significant potential for reduction of surface, line edge and line width roughness during the subsequent pattern transfer process. Since one of the underlying mechanism of roughness formation has been reported to be a synergistic effect of energetic ion bombardment, ultraviolet (UV) / vacuum ultraviolet (VUV) plasma radiation and increased temperature, a possible mechanism of organic mask curing may be the elimination of the above synergism by sequential exposures to VUV plasma radiation followed by ion bombardment dominated plasma etching. To examine this question, and establish the impact of pre-treatments on roughness introduction, etch resistance and pattern transfer fidelity during the pattern transfer process, we have studied pretreatments of 193nm PR and other organic masking materials in Ar and He discharges with pronounced UV/VUV emission. The impact of pretreatments and subsequent pattern transfer processes on the organic materials were monitored in real-time by in-situ ellipsometry. Multilayer modeling of these data allows determination of optical material density and film thickness of various layers, i.e. the surface layer densified by ion bombardment, the UV/VUV modified layer in the material bulk, and the rough surface layer. Additionally, post plasma characterization by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) provides information on bulk material modifications and surface roughness improvements, respectively. UV/VUV spectroscopy combined with Langmuir probe characterization provides information on plasma parametric dependencies of photon and ion fluxes, respectively. Pretreatments in a He discharge reduced roughness introduction in a C_4F_8/Ar pattern transfer process by ~50% (RMS=4nm) while increasing film etch resistance by ~30% leading to only a slight increase in the total material removal when compared to the uncured material (pattern transfer only). Time resolved studies of this process allow detailed investigation of distinct stages and underlying mechanisms of materials modification, such as radiation induced changes in the materials bulk, ion crust formation at the film surface, and surface roughness development. Correlating these observations with post plasma characterization by AFM and FTIR allows a mechanistic understanding of plasma based pretreatments or organic materials and their impact on the subsequent pattern transfer process. The dependence of improvements in masking performance on Ar and He plasma based pretreatments and a description of the underlying mechanisms will be presented.

5:00pm PS+SE-MoA10 Sub-32nm Node Mask Patterning for Deep Silicon Trench Etch, *J. Yarmush*, H. Haga, Y. Chiba, K. Kumar, P. Biolsi, TEL Technology Center, America, LLC, *J. An, H. Hichri, B. Dirahoui, X. Li*, IBM Microelectronics, *R. Wise*, IBM Research

In the last several semiconductor device generations, one of the complexities in fabricating ever smaller feature sizes and increased density, has been the stringent requirements placed on photolithographic processes and mask scheme formation. The use of Immersion Lithography, reduced resist layer thicknesses and planarity requirements have driven the need for complex multilayer-multimaterial stacks that can be utilized for subsequent plasma Etching masks.

One requirement by manufacturers of Sub-32nm DRAM technology, utilizing deep silicon memory cells, is an extremely high aspect ratio mask that enables the anisotropic etch profile of the Silicon Trench. To meet both the needs of the photolithographic processes and the high aspect ratio mask requirements of the Silicon Trench etch, a complex Photo Resist, Silicon Anti-reflective coating, Optical Dispersive Layer, CVD Oxide layer is used. This deposited mask stack also sits on top of a Silicon-on-Insulator layer that must also be etched through anisotropically.

In this paper, we describe the unique requirements of etching each film stack in order to meet the overall physical requirements of this high aspect ratio mask patterning etch. It also describes the process capabilities of a commercially available Capacitively Coupled Plasma reactor that enables it to meet these advanced complex film stack requirements.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Semiconductor Research & Development Center.

5:20pm PS+SE-MoA11 Quantitative Determination of the Mechanism of Anisotropic Silicon Etching, *M. Hines*, M.F. Faggin, K. Bao, A. Gupta, B. Aldinger, Cornell University

The production of atomically perfect surfaces by simple solutions is both intrinsically fascinating and technologically important. For over half a century scientists have known that many aqueous bases — so-called "anisotropic etchants" — selectively attack all silicon faces except Si{111}. As a result, a macroscopic silicon sphere placed into one of these solutions spontaneously transforms into a polyhedron. Twenty years ago, the surface science community was rocked when researchers at Bell Labs showed that, in some cases, the etched surfaces are not just smooth, they are atomically flat and passivated by a single monolayer of H atoms. This type of highly precise but inexpensive chemical machining is used in diverse applications ranging from the production of ink-jet nozzles to the fabrication of ultrasmall transistors to the cleaning and polishing of silicon wafers; however, the chemical reactions that govern this behavior remain a source of controversy. We resolve this controversy and give the first quantitative, atomic-scale understanding of anisotropic etching across all silicon surface — not just Si(111).

The reactivity of a wide variety of Si(100) surface sites towards a prototypical anisotropic etchant, ammonium fluoride, is quantitatively

determined from measurements of the atomic-scale morphology and chemical composition of etched surfaces. These measurements enable the effects of chemical strain, steric hindrance, and chemical structure to be separately determined. The high selectivity of the etchant is explained by the strain energy released during the chemical reaction; steric hindrance plays an important, but distinct, role. This pattern of reactivity is inconsistent with previously postulated mechanisms of aqueous silicon etching, which postulate insertion reactions across rigid, essentially immobile Si-Si backbonds. Instead, we propose that cleavage of the backbond occurs during the formation of a surface silanone which is driven by simultaneous interadsorbate strain release. On Si(100) surfaces, this hypothesis *quantitatively* explains the characteristic alternating-row etch morphology on both flat and vicinal surfaces, the observed site-specific reactivity, the unusual reaction kinetics, and the hydrogen termination of the etched surface without invoking an unreasonably strained reaction intermediate. This mechanism also explains the atomic-scale reactivity and relative etch rates of the three principal faces of silicon, thereby giving the first atomic-scale understanding of anisotropic silicon etching.

Tuesday Morning, November 1, 2011

Plasma Science and Technology Division
Room: 202 - Session PS+MN+TF-TuM

Plasma Processing for Disruptive Technologies
Moderator: M.C.M. van de Sanden, Eindhoven University of Technology

8:00am PS+MN+TF-TuM1 Scallop Free TSV Etching Method for 3-D LSI Integration, *Y. Morikawa, T. Murayama, T. Sakuishi, S. Toyoda, K. Suu*, ULVAC, Inc., Japan **INVITED**
Thru silicon via (TSV) etch process for deep and high-aspect ratio structure has been studied thoroughly for applications such as MEMS and CMOS devices. Recently, TSV used in 3D-LSI devices for logic devices may be a few microns in diameter and about 50 um deep. On the other hand, TSVs used in stacking memory devices, the via diameter and depth would be several tens of microns. Therefore, development of TSV etching process is very important for realizing these applications. In this study, a large via size etching in a high-pressure process was focused by using very high frequency capacitive coupled plasma (VHF –CCP) with an ultra self-confined system. This plasma system is simple parallel plate CCP about 100Pa or more process. High-pressure process was carried out on the plasma confined, because mean free pass is very short. And, ion energy distribution (IED) is also controllable by high-presser process with VHF bias. The bimodal IED changes under high-pressure. The peak of high-energy side is reduced, and a charge exchange peak appears. It is considered that the charge exchange is important to anisotropic Si etching of large size TSV with VHF bias.

And next, the high-density and small size of TSV below 10um diameter is indispensable to the utilization and improvement in high performance of 3D-LSI. We have developed a new etching system for TSV application for small size and high aspect ratio via. This system is a planer type magnetic neutral loop discharge (NLD) plasma. For high rate silicon etching, it is very important to understand not only the high density of the ICP plasma generation but also the high density of fluorine atoms. In this study, a novel RF antenna 'Multi Stacked rf Antenna' has been developed for highly accurate and high rate etching process. This antenna consists of multistage spiral turn rf antennas to reduce self-inductance (L). The L of this antenna is below 1.0 uH and it is a lower than the standard spiral antenna. As a result of performing the electron density measurement of the planer NLD plasma using this MS antenna, it succeeded in the high-density plasma production of $1x10^{12}$ / cm^3 by the process pressure of 7 Pa. Next, the Si etching process development was performed using the advanced NLD etcher. As a result, the etching rate improved 4 times more compared to the standard cylindrical NLD plasma. Finally, the diameter of 2um was attained by the anisotropic etching of 5 um/min, and the aspect ratio is above 10 using the planer NLD etcher. VHF CCP and planer NLD etching processes are non-cycle etch methods, and these processes were demonstrated about smooth sidewall TSV formation.

8:40am PS+MN+TF-TuM3 Deep Silicon Etching of 0.8 μm to Hundreds of Microns Wide Trenches with the STiGer Process, *T. Tillocher, W. Kafrouni*, GREMI, France, *J. Ladroue*, STMicroelectronics - GREMI, France, *P. Lefaucheux*, GREMI, France, *M. Boufnichel*, STMicroelectronics, France, *P. Ranson, R. Dussart*, GREMI, France
The STiGer process is designed to achieve high aspect ratio features in silicon. Like the Bosch process, passivation steps (SiF4/O2 plasmas) and etching steps are cycled to get vertical structures. The etching steps can be purely isotropic (SF6 plasmas) or anisotropic (SF6/O2 plasmas). It is required to cool the silicon substrate with liquid nitrogen to form a SiOxFy passivation layer. It desorbs and disappears when the substrate is heated back to room temperature. Thus, there is no need to clean neither the microstructures nor the chamber walls after each process run. Then, the robustness of the process is enhanced in comparison with standard cryoetching: the profiles are less sensitive to temperature or flow rate variations. But, like in Bosch etching, a scalloping is present on the sidewalls.

Submicron trenches having critical aperture of about 0.8 μm can be etched with high aspect ratios (> 40). In these cases, the average etch rate is around 1.8 μm/min. These features exhibit both undercut and a special defect, which is called "extended scalloping". This defect is composed of anisotropic cavities developed on the feature sidewalls, just below the mask. It originates from ions scattered at the feature entrance that hit the top profile and remove locally the passivation layer. This defect is observed only for high aspect ratios (typically above 10). Thus, we will also investigate the role of trench critical dimension (from 0.8 μm to 100 μm). A mechanism explaining the formation of the extended scalloping will be proposed.

We have studied the influence of both the duty cycle (tetch/(tetch+tpassivation)) and the chamber pressure on the profiles and the extended scalloping. Basically, when the duty cycle increases, etching dominates passivation, which leads to higher defects. Pressure is a way to tune the slope of the sidewalls. Actually, decreasing the chamber pressure helps to shift from positively tapered features to more vertical profiles, and even negative slopes, hence with dovetailed shape.

This will be correlated with plasma analysis by means of mass spectrometry and optical emission spectroscopy. Actually, it is relevant to investigate how changes in the plasma chemistry can modify the trench profiles.

These trends have been used to optimize two methods that can help to reduce the extended scalloping. The first consists in adding a low oxygen flow in the etch cycle, favouring a low additional passivation. The second technique consists in gradually increasing the SF6 flow from a low value to the nominal value. Consequently, the process starts with a low etch rate and a more efficient passivation, which helps to limit the extended scalloping.

9:00am PS+MN+TF-TuM4 Evaluation of Alternative Passivation Chemistries for TSV Applications, *E.A. Joseph*, IBM T.J. Watson Research Center, *G. Matsuura*, ZEON Chemicals L.P., *S. Engelmann*, IBM T.J. Watson Research Center, *M. Nakamura*, ZEON Chemicals L.P., *N.C.M. Fuller*, *E.M. Sikorski, M. Gordon, B.N. To*, IBM T.J. Watson Research Center, *H. Matsumoto, A. Itou*, Zeon Corporation
With the current advent of 3D integration for advanced interconnect and packaging applications, there has been a renewed focus on deep silicon etch technology to satisfy the need for Through Silicon Via (TSV) patterning. The most common etch method used to fabricate said devices is a time-muliplexed (BoschTM) process, based on years of maturity in the MEMS field.[i] However, issues such as scalloping, mask undercut and limited etch rates are becoming more pronounced as feature sizes scale to meet the ITRS roadmap requirements. This has prompted efforts to attempt to either develop a more conventional etch process[i][ii]or to modify the Bosch process to circumvent these issues.[iii][iv] [v] In this work, we explore a novel polymerizing feedgas chemistry for the deposition step of the Bosch process to improve mask undercut while simultaneously increasing TSV etch rate. Initial results indicate a 5x larger deposition rate as compared to C4F8 (under nominal conditions) and under optimized conditions, enables a 50% decrease in undercut along with 10% increase in TSV etch rate. Optical emission spectra also differ substantially between the two feed gases, indicating different dissociation pathways and radical densities. Further results and a detailed characterization of the deposition properties of the novel chemistry will also be discussed leading to a proposed mechanism for the profile improvements as compared to C4F8. [i] B. Wu, A. Kumar and S. Pamarthy, J. of Applied Physics 108, 051101 (2010) [ii] I. Sakai, N. Sakurai and T. Ohiwa, J. Vac. Sci. Technol. A 29(2), Mar/Apr 2011 [iii] N. Ranganathan et al, Proceedings of the Electronics Components and Technology Conference, 2005 [iv] H. Rhee et al, J. Vac. Sci. Technol. B 27(1), Jan/Feb 2009 [v] S.-B. Jo et al, J. Vac. Sci. Technol. A 23(4), Jul/Aug 2005

9:20am PS+MN+TF-TuM5 Wafer Scale Hermetic Packaging of MEMS, *C.S. Gudeman*, IMT **INVITED**
The explosion of MEMS in automotive and cell phone markets has been enabled by low cost wafer level packaging (WLP) technology that provides a robust and hermetic enclosure for an otherwise delicate device. The more obvious advantage of WLP is greatly improved reliability, because the device is protected from organic and particulate contaminants while in the hands of the end user. A less obvious advantage is the protection provided by WLP during the manufacturing process, which often produces the highest levels of stress that a MEMS device experiences. These processes include wafer grinding, wafer dicing, and chip solder re-flow attachment to circuit boards and other chips. Firstly in this talk, wafer level packaging technologies will be outlined, focusing on the truly hermetic methods -- alloy, glass frit, Au-Au thermo-compression, anodic, and fusion bonding. Secondly the integration of Through Silicon Vias (TSV) with WLP will be discussed. Finally the performance of these technologies will be compared from a manufacturing perspective, including yield and thermal budget.

10:40am PS+MN+TF-TuM9 Challenges in Plasma Etch for NVM: Scaling and Materials, *M. Kiehlbauch*, Micron Technology, Inc. **INVITED**

With advances in non-volatile memory, the major challenge confronting plasma etch is the introduction of new materials while simultaneously shrinking critical dimensions. This talk will address key development aspects including profile control, feature level uniformity, and plasma microdamage. Plasma microdamage is not the traditional, charge/voltage/current based impact to, for example, gate oxides. Rather, it is the changes to the atomic scale morphology in the sidewall or landing film of a plasma etch process. This results in a disruption of local stoichiometry, film defects, and other issues that impact device performance. The etch process and hardware changes to address this will be presented.

11:40am PS+MN+TF-TuM12 Mechanisms of Selective Etching for Magnetic Materials: Ni, Co and Ta Etching by Carbon Monoxide/Methyl Alcohol Based Plasmas, *K. Karahashi*, T. Ito, S. Hamaguchi, Osaka University, Japan

Dry etching of magnetic thin films is a crucial step in micro fabrication of magnetic random access memories (MARMs) and read/write heads for magnetic data storages. Argon (Ar) ion milling seems to be almost the only etching technique available in the current manufacturing processes. However Ar ion milling is incapable of achieving anisotropic and selective etching of magnetic films (Ni, Co etc.) over hardmasks (Ta etc.) and therefore highly selective reactive ion etching (RIE) of magnetic thin films is a highly sought-after technology. RIE processes based on CO/NH_3 or CH_3OH is a candidate for selective etching of magnetic thin films. In this study, we have examined etching processes of Ni, Co and Ta thin films by energetic CO^+, O^+ or OH^+ ions, which are considered to be major etchants of CO/NH_3 or CH_3OH plasmas. We have determined the etching yields and analyzed surface reactions, using a mass-selected ion beam system. The ion beam system is designed to inject mono-energetic single-species ions into a sample surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with an X-ray photoelectron spectroscopy (XPS) for in-situ chemical analyses of irradiated surfaces. The ion beam energy used in this study is in the range of 150-1000 eV. The etching yields are determined from measured depth profiles of irradiated surfaces and ion fluxes. The etching yields of Ni and Co by CO^+ ions are higher than that by O^+ ions but lower than the yields of possible physical sputtering, which are estimated from interpolation of sputtering yield data of inert atom ions (He^+, Ne^+, Ar^+, Kr^+ etc.). From XPS analysis for O^+ irradiated Ni and Co surfaces, oxidation is found to occur under O^+ irradiation, which suggests that the oxide layer hinders sputtering by ion bombardment. It is found that little oxidation occurs on Ni or Co surfaces under CO^+ ion irradiation and etching by CO^+ ion bombardments proceeds. On a Ta surface, on the other hand, in the both cases of O^+ and CO^+ irradiations, oxidation occurs and its etching yield is far smaller than the yield of its possible physical sputtering. Therefore we have found that high selectivity of Ni and Co etching against hard masks (Ta, TaN) arises from the prevention of sputtering by mask oxidation. Etching characteristics by OH^+ irradiation were also studied in a similar manner. This work was supported by the Semiconductor Technology Academic Research Center (STARC).

Plasma Science and Technology Division
Room: 201 - Session PS-TuM

Advanced BEOL / Interconnect Etching I
Moderator: A. Balakrishna, Applied Materials, Inc.

8:00am PS-TuM1 Narrow Pitch Dual Damascene Patterning using EUV Lithography in Association with a Spin-On Trilayer Resist System, *F. Lazzarino*, V. Truffert, B. Vereecke, S. Demuynck, IMEC, Belgium

Extreme ultraviolet lithography (EUVL) is one of the leading candidates for the 22-nm node device manufacturing. However, a major issue is the necessity to use thin photoresist (between 55-nm and 80-nm after development) because of resolution requirement and limited depth of focus. In addition, its low etch resistance does not allow high aspect ratio pattern transfer. In this context, a new hardmask strategy called spin-on trilayer resist system has been considered.

In this work, we mainly focus on the etch patterning capability of narrow pitch dual damascene structures by using EUVL combined with a spin-on trilayer resist system. The latter consists of three layers. The photoresist on top is used to pattern a thin spin-on glass layer which is then used to pattern a thick spin-on carbon layer (SOC). The SOC has two functions. It is used

for its good gap-filling capability to avoid patterning over nonplanar surfaces but it also acts as a hardmask to pattern the dielectric stack (150-nm of oxide on top of 15-nm of SiCO and 5-nm of SiCN). Regarding the dual damascene architecture, two different approaches have been considered: the via-first and the trench-first. Despite few challenges such as the well-known fencing issue, the via-first approach has been chosen as it is less sensitive to misalignment. In this scheme, two lithography and etch steps are needed, first to form the via then to pattern the trench and etch the barrier layer. In this study, we compared the via opening by using the standard PECVD carbon layer and by using the SOC layer. As expected, the PECVD carbon layer has a better process window compared to the SOC layer. The selectivity is greater and allows many chemistry variations to fine tune for instance the profile. To get similar process window with the trilayer resist system, we introduced C4F8 and CO to substitute C4F6 and O2 in the original chemistry. This modification clearly improved the process by having a better control on the passivation layer formation. Regarding the trench opening, we observed a significant line wiggling of the SOC hardmask for 50-nm half-pitch structures and beyond. We characterized this instability thanks to stress measurements and we kept it under control by changing three different process parameters: the bottom electrode temperature, the baking conditions after coating and the film thickness. Each of them has an impact but the best result came from combining all three together.

To conclude, we demonstrated that narrow pitch dual damascene structures can be obtained by using EUVL in association with a spin-on trilayer resist system. The structures formed in this way shows good electrical characteristics.

8:20am PS-TuM2 TiN Hard Mask Integration Line Wiggling Onset: Etching Time Dependence, *G.A. Delgadino*, Lam Research Corp.

Cu resistivity increase at smaller geometries and the use of lower κ dielectrics forced several changes on BEOL integration. Susceptibility of ULK material to strip damage drove the adoption of TiN hard mask integration starting with a few players at 65nm node to full adoption at 32nm for advance logic.

TiN hard mask demonstrated good selectivity during dielectric etch but concerns arise as we move to smaller pitch: 1- TixFy residues may compromise metallization of small features and 2- Residual compressive stress in the TiN may induce line wiggling. This last concern is the focus of this work.

We develop a simple analytical model based on Energy balance to predict wiggling onset based on geometrical and mechanical properties of the materials. We showed that the wiggling onset aspect ratio reduces with the pitch. We also shown that even when at the end of the process the no-wiggling condition is satisfied, wiggling might have occurred during etch causing feature distortions.

8:40am PS-TuM3 Surface Reaction Control for BEOL Application, *M. Fukasawa*, T. Tatsumi, Sony Corporation, Japan **INVITED**

Increasingly there are more challenges of controlling the plasma processes for BEOL integration, which include the Cu/low-k interconnects, contact hole etching, etc. The presentation will give an overview of the surface reaction control during plasma processes. The main focus is damage reduction and suppression of process fluctuations.

Reducing the damage to low-k dielectrics caused by plasma exposure is one of the key issues. O_2-based plasma has been widely used for ashing the photoresist on low-k SiOCH. H_2-based plasma is employed for the etching of organic low-k film as well as the ashing of photoresist. The origin of damage generation is classified by ions, radicals, and UV/VUV radiation. It was found that not only the ions but also the synergy of radicals and UV/VUV radiation cause a significant amount of damage in the SiOCH, measured by using the pallet for plasma evaluation (PAPE).[1] Hence, precise control of incident ions, radicals, and UV/VUV radiation is required for controlling the surface reactions.

In addition to the precise control of incident species, the optimization of subsequent processes (wet treatment, annealing, etc.) are very important to obtain sufficient electrical yields and reliabilities. The remaining damaged layer after wet treatment degrades the Cu and SiOCH surface and corrupts the interface between the Cu and barrier metal. For instance, the desorbed H_2O from the SiOCH damaged layer causes the oxidation of barrier metal, which results in a shorter EM lifetime. The surface modification during SiCN and SiN etching by CH_xF_y-based plasma and its impact on the electrical yields will also be discussed.

The suppression of fluctuation is also required in the advanced interconnects. Although statistical prediction is one of the approaches to realize stable processes, there is a limitation of prediction accuracy for purely statistical predictions due to the lack of physical models. Thus, the

combination of statistical and physical models for highly accurate prediction has become an emerging trend in mass production. We will demonstrate a novel statistical etch rate prediction model by considering the fluctuation caused by the plasma-wall interactions.[2]

The developed prediction model is one of the approaches to realize stable processes. Changes in the spatial distribution of reactive species in the etching chamber are, however, very difficult to detect in current mass production tools. Thus, greater progress of the *in-situ* monitoring tools and prediction methods based on the physical model (simulation) are strongly required in the near future.

1. S. Uchida et al., JAP 103, 073303 (2008).

2. M. Fukasawa et al., JJAP 48, 08HC01 (2009).

9:20am PS-TuM5 Trench First Metal Hard Mask RIE for the 22 nm Node and Beyond, *Y. Feurprier*, R. Gaylord, Y. Chiba, K. Kumar, D. Trickett, TEL Technology Center, America, LLC, Y. Mignot, ST Microelectronics, R. Srivastava, T. Kwon, R. Koshy, C. Labelle, GlobalFoundries, Y.J. Park, Samsung, E. Wormyo, S. Allen, IBM Research, E. Soda, Renesas Electronics, D. Horak, Y. Yin, J. Arnold, IBM Research, M. Ishikawa, H. Tomizawa, Toshiba America Electronic Components
Trench First metal Hard Mask (TFmHM) integration scheme for BEOL has gained traction over recent years because it can mitigate many challenges that are inherent with Via First Trench Last (VFTL) scheme. This integration scheme was more recently shown to enable Self-Aligned Via (SAV) patterning. The SAV patterning implies a pretty drastic change of the via process as, on top of the usual via requirements, the via patterning process needs to be selective to the metal HM. Key process parameters including temperature, gas chemistry, power and pressure were investigated. The required selectivity of the materials and tight CD control capability necessitate temperature controllable chucks eventually allowing greater process flexibility for both via and trench patterning.

The simultaneous control of via, trench and chamfer profiles (i.e. Critical Dimensions, depth, taper profile, etc), implies the need for better control of the metal HM selectivity during both SAV and trench patterning and the need for flexible adjustment of the ion energy and control of the flux of ions and active neutrals. Low-k material damage control is always pertinent in the RIE process as dimensions get smaller. As the direct result of such tight process guidelines, the hardware challenges arise and new dimensions in process controls are needed.

In this paper, the RIE efforts on process controls of the via and trench profiles, the metal HM selectivity, associated hardware solutions and future process flow options under TFmHM scheme will be discussed.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Research Alliance Teams in Albany, NY 12203. This work has also been supported by the independent Bulk CMOS and SOI technology development projects at the IBM Microelectronics Div. Semiconductor Research & Development Center, Hopewell Junction, NY 12533.

9:40am PS-TuM6 Plasma Processing of Ti and TiN Metal Hardmasks for Dielectric Etch, *F. Weilnboeck**, E. Bartis, S. Shachar, G.S. Oehrlein, University of Maryland, College Park, D. Farber, T. Lii, C. Lenox, Texas Instruments Incorporated
Ti and TiN metal hardmasks are of interest for plasma-based pattern transfer into low-k materials due to their expected improvements of etch performance and process flow relative to resist masks. We have studied the performance of Ti and TiN in CF_4/Ar and C_4F_8/Ar discharges along with organosilicate glass (OSG) - a reference low-k material. Plasma processes were characterized in real-time by in-situ ellipsometry and provided information on erosion stages, etch rates (ER) and selectivity (SEL), i.e. ER(OSG)/ER(hardmask). Post plasma characterization was performed by vacuum transfer x-ray photoelectron spectroscopy (XPS). Plasma parameters investigated were: 1) ion energy, 2) pressure, 3) Ar dilution, 4) O_2 addition and 5) N_2 addition to fluorocarbon/Ar mixtures. Furthermore, we have studied chamber wall contamination and surface reactions upon atmospheric exposure of processed Ti/TiN hardmasks. Ellipsometric multilayer modeling of real-time measurements showed three hardmask erosion stages: 1) initial removal of surface oxides, 2) steady state erosion with F-saturated hardmask surfaces (TiF_x, x~3) covered with a FC film (0.8-1.6nm depending on plasma conditions) and 3) small amounts of Ti remaining on the underlayer after erosion of the hardmask layer. For all plasma conditions, Ti provides systematically lower ERs and higher SELs (~15) than TiN (~11). The higher ERs of Ti over TiN can be explained by the rapid removal of N by formation of NF_3 and the smaller Ti-atom number density of TiN compared to Ti. Surprisingly, the more polymerizing

C_4F_8 conditions lead to lower SELs than CF_4. This observation is explained by FC layer-induced OSG ER reduction, whereas for the hardmasks materials ER are limited by product volatility and the FC surface layer effect is reduced, e.g. as compared to conventional organic masking layers. Chamber contamination studies have shown that only small amounts of Ti (<1%) are deposited together with FC on the chamber wall. Overall, metal hardmasks, especially Ti, showed excellent performance as a masking material in low-k etch and provide high SEL (~15) which can be further increased by systematically optimizing discussed plasma parameters.

11:00am PS-TuM10 Superposition of High Negative DC Voltage in Capacitively Coupled Plasma, *A. Ranjan, A. Metz, A. Lisi, Y. Chiba, W. Li, Y. Feurprier, K. Kumar, P. Biolsi, TEL Technology Center, America, LLC, L. Chen, P. Ventzek, R. Sundararajan, Tokyo Electron America
The effects of applying a negative DC voltage to capacitively coupled plasmas (CCP) were investigated using PIC-MCC simulation and experiment. High energy secondary electrons, originating at the electrode with high negative DC voltages (DC electrode), are generated due to ion impact as well as electron-impact. These secondary electrons are accelerated away from the DC electrode by the sheath voltage drop. These secondary electrons gain energy equal to DC voltage drop across the sheath and travel to wafer electrode or get trapped between electrodes. Trapping and dumping of ballistic electrons depends on the voltages on the electrodes. Ballistic electrons alter the bulk electron energy distribution function of the plasma (EEDF), EEDF at wafer, high energy electron flux to wafer and plasma density profiles. Simulation shows that center to edge uniformity, plasma density and EEDF can be tuned by applying negative DC voltage in CCPs. Bulk plasma volume can be modulated by applying negative DC voltage giving us a very effective knob for an "effective" variable gap CCP without moving chamber parts in vacuum. The change in EEDF alters the plasma chemistry, the result of which can be observed by optical emission spectra and blanket etch rate data, validating the changes in chemistry due to superimposed negative DC voltage. Various other interesting aspects will also be presented.

11:20am PS-TuM11 Evaluation of C5HF7: A High Etch Selectivity Hydrogen-Containing Fluorocarbon Gas for Oxide Etch, *R.L. Bruce*, IBM T.J. Watson Research Center, M. Nakamura, ZEON Chemicals L.P., S. Engelmann, E.A. Joseph, IBM T.J. Watson Research Center, G. Matsuura, ZEON Chemicals L.P., N.C.M. Fuller, E.M. Sikorski, W.S. Graham, Y. Zhang, IBM T.J. Watson Research Center, A. Itou, Zeon Corporation
A high etch selectivity hydrogen-containing fluorocarbon gas, C5HF7, was evaluated for high aspect ratio dielectric etch. Plasma etching with Ar/C5HF7/O2 chemistry was shown to have significant advantages over Ar/C4F6/O2 in terms of oxide-to-organic mask etch selectivity and line-edge roughness. The mechanism behind the high etch selectivity of C5HF7 originated from the different thickness and composition of steady-state fluorocarbon (FC) layers generated on oxide and organic mask materials during plasma etch. We also determined that hydrogen addition to the Ar/C4F6/O2 feedgas did not reproduce C5HF7 etch behavior, presumably due to the difference in atomic hydrogen formation between molecular H2 dissociation versus intramolecular H dissociation (from C5HF7). This latter phenomenon facilitated a wider window for "etch stop" margin. Profile evaluation showed larger bowing for C5HF7, compared to C4F6, and was linked to a higher sticking coefficient of CxFyHz radicals. This was verified and remedied by increasing the substrate temperature, which reduced the radical sticking coefficient and eliminated bowing, while maintaining the high etch selectivity. We also demonstrated reduced low-frequency line-edge roughness when etching with C5HF7. We showed that less surface roughness was generated using C5HF7 since less organic mask thickness was removed. In addition, since a major contribution of line-edge roughness was the transfer of organic mask surface roughness into the sidewalls of the dielectric, overall lower line-edge roughness was observed.

11:40am PS-TuM12 Etch Uniformity Improvement Using Mid-Gap Capacitively Coupled Plasma, *C. Cole*, A. Ko, A. Ranjan, T. Enomoto, A. Metz, K. Kumar, P. Biolsi, TEL Technology Center, America, LLC, E. Wornyo, H. Yusuff, S. Allen, R. Wise, IBM Research, C. Labelle, T. Chen, GlobalFoundries, S. Kanakasabapathy, IBM Research, Y. Mignot, STMicroelectronics
As device dimensions continue to shrink, uniformity of etch rate/feature depth and critical dimension becomes very important. Capacitively coupled plasma (CCP) sources have advantage in terms of uniformity over non-planar sources in addition to design simplicity, reliability and wide process window. Wide-gap CCPs have been used for front-end etch applications where as small-gap CCPs are work-horse for back-end dielectric etch. Recently, studies on mid-gap CCPs indicates that inter-electrode spacing of ~100mm is best suited for etch rate and CD uniformity. In our studies, for tri-layer mask etch and TiN hard-mask etch, mid-gap CCP achieved

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* Coburn & Winters Student Award Finalist

uniformity of <1nm (3σ) CD and ~1% (3σ) etch rate. Mid-gap CCPs have 20-30% higher etch rate compared to wide-gap CCPs. Power on top electrode can be divided to center and edge for control of plasma density distribution. Design changes in pumping port assembly effectively create uniform confined plasma without plasma leaking through pump-port. Plasma confinement helps in creating denser plasma at relatively lower RF power. Using above-mentioned "knobs", flat etch rates and CDs were achieved in mid-gap CCPs.

Tuesday Afternoon, November 1, 2011

Plasma Science and Technology Division
Room: 202 - Session PS1-TuA

Advanced BEOL / Interconnect Etching II
Moderator: S. Sriraman, Lam Research Corp.

2:00pm PS1-TuA1 Feature Profile Evolution for HARC Etching in SiO₂, *P. Moroz*, Tokyo Electron US Holdings Ltd., *S.-Y. Kang*, Tokyo Electron Ltd., Japan

Feature profile control for HARC etching is a very important issue. Possible profile defects such as bowing, necking, variations in depth and shape, among others, become critical for the next technological steps with ever shrinking dimensions of the features. Using numerical simulations as a tool, we studied HARC etching of SiO2 by the fluorocarbon-argon-oxygen plasma in a capacitive-type plasma system. The first step in our simulations involved estimation of neutral and ion fluxes, and their angle-energy distributions for most important species involved into processing in the systems chosen for comparison. Then the feature profile simulator FPS-3D [1] was run to estimate various chemical and physical effects on HARC profile evolution during processing. The difficult part in those simulations was taking into account deposition of polymer films and etching through those films. The final results come as a competition between counteracting effects of etching and deposition. Important effects of ions for etching at the bottom of the contact holes, and of polymer films for protecting sidewalls from further etching, were investigated. Possible bowing and necking effects were considered in detail. Calculations were carried out for different sizes of the features, different gas compositions, and different RF powers leading to different ion energies. Published data for the underlined reaction mechanisms were analyzed and used for tuning the chemical reactions database in the FPS-3D code. Comparison of simulations with different experiments and the corresponding analysis of HARC etch processing are presented. The authors are thankful to Masanobu Honda and Akira Tanabe for providing experimental data.

[1] P. Moroz, 57th AVS Int. Symp., PS1-ThA10, Albuquerque, NM, October, 2010.

2:20pm PS1-TuA2 Hybrid Strip Process to Minimize Low-k Dielectric Damage, *E.A. Hudson*, *T. Choi, K. Takeshita, S. Sirard, B. Ji, M. Kato, M. Moravej, O. Turmel, G.A. Delgadino, S. Heo, A.D. Bailey III*, Lam Research Corp. **INVITED**

Integration of materials with low dielectric constant into microelectronics interconnect structures has presented significant challenges for several years. As structures and materials have evolved, there has been a consistent concern that plasma processing damages the low-k material, especially during process steps intended to strip organic mask films. For efficiency, it is convenient to remove organic films *in situ,* as part of a sequence of etch steps in the etch reactor. But plasma strip conditions may remove carbon from the dielectric film, causing an increase in dielectric constant and other issues. This is an increasing concern as the target dielectric constant is reduced with successive device generations, and the films become more sensitive.

For via-first integration schemes which use an embedded metal hard mask to define the trench pattern, organic mask stripping is required only after the vias are partially defined in the dielectric. This approach protects the trench sidewall by eliminating the post-trench strip, but may lead to localized regions of dielectric damage in the final structure, corresponding to the remaining material which was exposed to post-via strip.

For *in situ* plasma strip processes based upon CO2 gas, damage to the dielectric film is mainly induced by reactive neutral species at the via sidewall. There are several strategies to reduce this damage while maintaining the ability to strip the targeted organic mask layer. One is to minimize the radical to ion ratio, in order to reduce the damage rate while preserving strip rate. Another method is the "hybrid strip" in which a protective layer of polymer is deposited on the via sidewall prior to strip. This barrier reduces the influence of strip plasma species on the underlying dielectric film. Damage reduction is achieved using passivation based either upon hydrocarbon or fluorine-containing polymers.

Because the strip plasma tends to remove the passivation from the sidewall, and because the damage rate increases in the final part of the strip process, better results can be achieved if the protective films is periodically re-applied. A cyclic process which alternates between passivation and strip conditions minimizes the strip-induced damage at the via sidewall. To facilitate an efficient hybrid strip process, the etch reactor design can be optimized for rapid switching between the two different plasma conditions.

This requires minimization of both the gas exchange time and the RF coupling stabilization time.

3:00pm PS1-TuA4 Model for High Aspect Ratio Dielectric Etch Process in a Capacitively-Coupled Plasma, *J.A. Kenney*, *A. Balakrishna, A. Agarwal, N. Misra, S. Rauf, K. Collins*, Applied Materials, Inc.

Etching of high aspect ratio (HAR) features in dielectric substrates is a challenging process, growing increasingly difficult with each new device generation. A common approach uses a multi-frequency capacitively-coupled plasma (CCP) reactor with high bias power and a dilute mixture of fluorocarbon and oxygen feed gases. Here, F atoms are the primary etchant, assisted by high energy ions to penetrate the fluorocarbon polymer layer formed by CFₓ radicals. [1] Oxygen atoms act to suppress excessive polymerization. The high energy ions give directionality to the etch process, with sidewalls remaining protected by the fluorocarbon polymer.

Due to the complexities involved in developing processes for each new application, many efforts have been made to model HAR etch processes (e.g., [2]). These necessarily involve at least two fundamental parts: (1) a plasma model of the CCP, which ideally includes the effects of power, generator frequencies, gas composition and flow, pressure, and reactor geometry, and (2) a model of the surface mechanism, which considers fluxes of relevant species, ion energies, and a simplified description of the competing deposition and etching processes. Complicating matters are the difficulties in obtaining systematic experimental data by which to validate either model so as to gain confidence in their predictive capabilities.

In this paper, we present models of an HAR dielectric etch process in a CCP, where the surface mechanism has been developed using experimental etch rate data generated on blanket oxide wafers. We focus on low pressure processes in an Ar/C₄F₆/O₂ mixture, using a multi-frequency CCP with very high frequency (VHF) source and dual radiofrequency (RF) bias. Experimental data were collected for multiple pressures (15 – 80 mT), source powers (500 – 900 W), bias powers (3500 – 7100 W in different frequency mixtures), and flows of feed gases. The same processes were modeled using CRTRS, Applied Materials' 2/3D reactor-scale plasma simulation tool, giving fluxes and energies of etch-relevant ion and neutral species. A surface mechanism based on that of Schaepkens et al. [1] was then developed, using the plasma simulation output and experimental etch rate data for calibration of parameters. Finally, this mechanism was used in a string-based feature profile evolution tool to quantify the impacts of varying the above process parameters.

[1] Schaepkens et al., JVSTA 17, 26 (1999).

[2] Stout et al., AVS 56th International Symposium, San Jose (2009).

4:00pm PS1-TuA7 Plasma-induced Damage Reduction in Porous SiOCH Dielectrics by Replacement of H₂ and N₂ by CH₂F₂ and Ar in Fluorocarbon Based Plasmas, *L. Souriau*, *F. Lazzarino, L. Carbonell, I. Ciofi, P. Verdonck, J.F. de Marneffe, M. Baklanov*, IMEC, Belgium

With the scaling of devices and related interconnects, the integration of dielectric materials with a k-value lower than 2.5 is greatly required. In particular hybrid porous SiOCH low-k materials are considered as promising candidates. However, such low-k dielectrics generally have a poor resistance to plasma damage due to their high connected porosity. It is therefore important to develop less damaging etching chemistries as well as more resistant low-k materials. During the discharge, ion bombardment, active radicals and VUV radiations are responsible for the degradation of the low-k. Mainly, -CH₃ groups are removed from the film resulting in its hydrophilization and consequent moisture uptake which has a severe impact on the final k-value after patterning.

In order to limit the damage during plasma etch, fluorocarbon-based chemistries allow a thin protective etch polymer film to be deposited on the surface of the low-k film during plasma etch and therefore effectively prevents possible damage by penetration of active radicals. We have evaluated the etching of a SiOCH dielectric with a k value of 2.0 using CF₄ in combination with either C₂H₄ or CH₂F₂ and using H₂, N₂ or Ar as tuning gas. The plasma damage has been evaluated by measuring the loss of –CH₃ groups and –OH uptake by FTIR and by measuring the k-value variation by forming MIS planar capacitor. Starting from a CF₄/H₂/N₂ plasma, it has been found that the damage is reduced by substituting H₂ by N₂. H is able to diffuse deep into the low-k film and probably remove –CH₃ groups by forming CH₄. Switching to a CF₄/C₂H₄/N₂ plasma further allows to decrease the damage, most probably through the formation of a thicker passivation layer on the low-k. Plasma damage can be further reduced by replacing N₂ by Ar, leading to a CF₄/C₂H₄/Ar plasma. Possibly, N₂ is causing damage by extracting C from the low-k film by forming HCN by-product. However the replacement of N₂ by Ar resulted in a reduction of the etch rate which could

be recovered by finally replacing C_2H_4 by CH_2F_2 while maintaining a low damage level.

Finally, 90nm half pitch trenches have been patterned into the SiOCH dielectric film using a dual hard mask approach (spin-on glass and spin-on carbon films). The influence of the hard mask on the plasma composition required optimization of the etch conditions in order to obtain straight profiles. Integrated k-value after complete processing will be discussed.

In conclusion, we have showed that H_2 and N_2 were responsible for the low-k damage during etch in flurocarbon based plasmas. Switching to a $CF_4/CH_2F_2/Ar$ plasma allows to reduce damage while maintaining good patterning capability.

4:20pm PS1-TuA8 Using Pulsed Power to Control Etch Properties of SiO_2 in $Ar/CF_4/O_2$ Capacitively Coupled Plasmas, *S.-H. Song*, *M.J. Kushner*, University of Michigan

Feature scale etch or deposition properties in plasma processing of microelectronic devices are determined by the energies and fluxes of radicals and ions to the wafer. These fluxes are ultimately controlled by controlling and customizing the electron energy distribution function $f(\varepsilon)$ which determines the dissociation patterns of feedstock gases and the relationship between applied power and sheath potential. One way to customize $f(\varepsilon)$ in dual frequency capacitively coupled plasmas (CCPs) is using pulse power for either or both of the high frequency or low frequency. Pulsed power in CCPs is attractive for controlling $f(\varepsilon)$ and plasma properties as it provides a means for producing combinations of fluxes (e.g., magnitude, identity and energy) not otherwise attainable using continuous wave excitation. In these systems, the choices of duty cycle and pulse repetition frequency (PRF) are important in determining the cycled average value of $f(\varepsilon)$ and $f_I(\varepsilon)$ due to the role of thermalization of electrons during the afterglow. The ability to control $f(\varepsilon)$ and $f_I(\varepsilon)$ may have both clear and subtle effects on the critical dimensions (CD) of etch features. For example, charge accumulation in the feature and the angular spread of ions may be controlled by the choice of duty cycle and PRF, both of which affect the etch profile. This enables some ability to control, for example, the sidewall slope of high-aspect-ratio (HAR) features by pulse-power formats. To demonstrate the ability to control feature profiles through control of $f(\varepsilon)$ and $f_I(\varepsilon)$ using pulsed plasmas, simulations were performed separately in two regions – on the equipment scale using the Hybrid Plasma Equipment Model (HPEM) and on the feature scale using the Monte Carlo Feature Profile Model (MCFPM). The fluxes of radicals and ions to the wafer from the HPEM are transferred to the MCFPM to calculate the etch properties. Plasma properties, $f(\varepsilon)$ and $f_I(\varepsilon,\theta)$, and ratios of fluxes to the wafer for an $Ar/CF_4/O_2$ gas mixture in a 2-frequency CCP will be discussed. The tuning of etch rates and profiles of HAR features in SiO_2 resulting from these fluxes will then be summarized.

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

4:40pm PS1-TuA9 Chemical Mechanisms for Dielectric Product Development, *A. Balakrishna*, A. Agarwal, J.A. Kenney, S. Belostotskiy, S. Rauf, K. Collins, Applied Materials, Inc.

Smaller technology nodes in the semiconductor industry place increased emphasis on etch productivity requirements, such as etch rate and critical dimension. Modeling and simulation is playing a central role in new developments (design of new hardware and exploration of novel processing options) to address the concurrent demand for improved performance and shorter development cycle. Validation against experimental data is a critical step in making these models a mature development tool. Monte Carlo, level set and string based feature scale models have been used to investigate processing issues within nanoscale features. Due to the complexity of surface and sub-surface processes, these models generally use empirically developed mechanisms which fit the model predictions to measured profiles and film characteristics. In this paper, we apply and refine the above method to develop a validated dielectric etch mechanism and feature scale model.

We obtained experimental data for etching of blanket SiO_2 wafers in a c-$C_4F_8/O_2/Ar$ plasma over a wide range of pressures (25-150 mTorr), bias powers (500-1500 W), and c-C_4F_8 and O_2 flows in a dual-frequency capacitively coupled plasma etcher. The etch rate increased with bias power and c-C_4F_8 flow rate, weakly decreased with increasing O_2 flow rate, and moderately increased with pressure. The reactor scale simulations were performed using CRTRS, a 2/3-dimensional fluid plasma model. The plasma simulations provided fluxes of various fluorocarbon polymerizing species, atomic oxygen and atomic fluorine. We also calculated fluxes and energies of the ions impacting the wafer. These values were used to calibrate an etch mechanism, whose main features are (a) a polymer thickness determined by the balance between polymer deposition (by C_xF_y species) and polymer removal (by ion sputter and O etch), (b) an exponential decay in ion energy through the polymer, and (c) reactive ion etching at the polymer-dielectric interface.[1] The etch rates and their trends

with bias power, c-C_4F_8 flow rate and O_2 flow rate were captured well in this model. The calculated polymer thicknesses also exhibited the expected trends, decreasing with bias power and O_2 flow rate and increasing with c-C_4F_8 flow rate. Our mechanism was not able to capture the etch rate trends with pressure, which is likely due to deficiencies in our plasma chemistry mechanism for $Ar/c-C_4F_8/O_2$ gas mixture. Finally, the calibrated mechanism was used in a string based feature profile model to investigate the influence of control parameters on dielectric etch process in a dual-frequency capacitively coupled plasma tool.

[1] Schaepkens et al, JVST A, 17, 26 (1999).

5:00pm PS1-TuA10 Optimization of CF_3I Process for Low-K Etching, *A.J. Gildea, J.C. Long, E. Eisenbraun*, College of Nanoscale Science and Engineering, the University at Albany-SUNY, *V. Omarjee, F. Doniat, N. Stafford, C. Dussarrat*, American Air Liquide – Delaware Research and Technology Center

Semiconductor manufacturing is facing major integration challenges. The introduction of ultra low-k materials (k=2.5 and below) in BEOL processing combined with the always shrinking dimensions increased the number of film parameters such as LER or species diffusion that need to be perfectly mastered. In particular, the use of porous dielectrics to reduce permittivity is done at the expense of film chemical and mechanical robustness. With films having porosity ranging from 15 to 30%, patterning collapse, impurity diffusion and other defects are becoming serious issues. A negative impact on interconnect reliability and performance is observed unless tight process controls and/or new approaches are employed. To overcome the defects created during the low-k patterning, one approach that is considered here is the use of new etch gases. Among the possible choices, CF_3I has seen increased momentum over the past years. When the first studies >10 years ago demonstrated some interesting features of CF_3I such as a GWP<1, the benefits were still too marginal to consider a fundamental change for dielectric etching in the semiconductor industry. Recently, with the increasing challenges to be overcome when etching the low-k, alternatives such as CF_3I are receiving increased attention.

In this talk we will present a comparison of the etching performance such as etch rate and selectivity of CF_3I alone or in combination with standard fluorocarbons such as CF_4 and C_4F_8.

Etching rate measurements performed on blanket porous low-k films (k=2.4) showed comparable values between CF_3I and the standard gases; therefore demonstrating no loss of throughput. Possible iodine incorporation during the process was carefully monitored and found to be negligible. Iodine, if detected, is usually at the detection limit of the tools (<0.4 at.%) and concentrated at the film surface therefore could be easily removed during the subsequent ashing and cleaning steps.

Patterned structure etch testing was performed and optimized using a DOE approach. CF_3I was found to be suitable to obtain nicely etched features. In many cases, better etched structures and higher selectivity were obtained using CF_3I compared to the standard gases.

5:20pm PS1-TuA11 Mechanism of Highly Selective SiO_2 Etching over Si_3N_4, Si and Photoresist Using Hydro-Fluorocarbon Gases, *Y. Miyawaki, Y. Kondo, K. Asano, M. Sekine, K. Ishikawa, T. Hayashi, K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan

Highly selective etch of dielectric films is one of the key technologies in integrated circuits fabrications. We achieved extreme high SiO_2 selectivity against Si_3N_4, Si and ArF photoresist using hydro-fluorocarbon gas, C_5HF_7 and O_2, Ar gas mixture [1] in a dual frequency (60 MHz / 2 MHz) capacitively coupled plasma (CCP). The selectivity over Si_3N_4 seemed to be infinite because selective fluorocarbon deposition occurred on Si_3N_4. The surface roughness that leads to line edge roughness was reduced by the selective deposition. The selective etch mechanism among plasma etch using fluorocarbon gases with and without hydrogen in gas molecule was investigated by the diagnostics of gas phase species and etched surfaces. As comparing CxFy, CxFyO and CHxFy gases, it was found that the hydrogen containing species with larger molecular weight play an important role for forming thick and carbon-rich polymer film especially on Si_3N_4, as well as on Si, photoresist. For the CHxFy gas plasma, the density of F radical that degrades the selectivity was inclined to be lower. CHxFy species act as an etchant for SiO_2 that contains oxygen, similar to the conventional selective etch scheme of SiO_2 by fluorocarbon plasma [2]. On the other hand, it could be deposition species to reduce the etch rates after some etch reaction on the surfaces of Si_3N_4, Si and photoresist that have no or less oxygen content. This means that the CHxFy species are etchants at the very beginning and turn to species for fluorocarbon polymerization just on Si_3N_4, Si and photoresist. Here, we need some sacrifice layer to initiate that selective deposition. The photoresist surface suffered roughness formation in the beginning, then the roughness was cured by the further deposition with ion bombardment [3]. This protective and roughness curing deposition on photoresist should occur for CxFy gas plasma in some condition (e.g. higher

gas-mixing ratio of CxFy/Ar), however it also forms a thick polymer on SiO_2 to stop etching. The temperature dependence for the etching and deposition properties [4] suggested that the difference of sticking coefficient for species with and without hydrogen was not so important. It is also speculated that the thick polymer formation on Si_3N_4, Si and photoresist while less reducing the SiO_2 etch rate is due to the relative large flux of specific hydrogen containing species in C_5HF_7 plasma.

Acknowledgement: Tokyo Electron Ltd., ZEON Corp., JSR Corp.

References: [1] Y. Miyawaki, et al.; Proc. 32nd Int'l. Symp. Dry process, P.181 (The Japan Society of Applied Physics, Tokyo, 2010). [2] M. Sekine; Applied Surface Science **192**, (2002) 270. [3] K. Asano, et al.; The 72nd Fall Meeting of JSAP, 31a-M-6 (The Japan Society of Applied Physics, Yamagata, 2011). [4] Y. Miyawaki, et al.; ibid., 31a-M-4

Plasma Science and Technology Division
Room: 201 - Session PS2-TuA

Plasma Diagnostics, Sensors and Control I
Moderator: V. Nagorny, Mattson Technology, Inc.

2:00pm PS2-TuA1 Prediction of Ion Sheath Shape and Ion Trajectory during Plasma Etching Processing using On-Wafer Monitoring Technique, *R. Araki, K. Miwa, T. Kubota,* Tohoku University, Japan*, T. Iwasaki, K. Ono,* Mizuho Information & Research Institute, Inc., Japan*, S. Samukawa*, Tohoku University, Japan
Precise plasma processes are indispensable for the fabrication of ULSI and MEMS devices. Some MEMS devices have larger scaled 3D structures comparable to the ion sheath thickness on the surface in plasma processing. In such cases, because of distortion of sheath shape due to the MEMS structure, ions trajectory are distorted to the surface and it causes etched shape anomaly. In order to solve these problems, we are developing a system to measure sheath thickness and to predict sheath shape, ion trajectory, and etched shape by fusion of a new on-wafer monitoring data and computer simulation. Our newly developed on-wafer sheath shape sensor can measure the surface potential and ion saturation current at wafer surface. Based on these results, the sheath thickness, shape, and ion trajectory were calculated by using our developed simulation. In this study, we could measure the sheath thickness, and then calculate the sheath shape deformation around a structure having large step in the case of using SF6 inductively coupled plasma. We found that the sheath thickness was about 1 mm and ion trajectory was bent near the large steps on the wafer surface. This result was completely corresponding to the actual etching pattern profile near a structure having large step. It is suggested that our proposed fusion system of on-wafer monitoring data and computer simulation is very effective to predict real etched shape during plasma etching processes.

2:20pm PS2-TuA2 Measuring Electron Density, Electron Temperature, and Plasma Potential with RF Frequency Probes, *D.R. Boris, R.F. Fernsler, S.G. Walton*, Naval Research Laboratory (NRL)
Plasma density measurements are an essential tool in understanding and controlling processing plasmas across a wide range of applications. Charge collection probes (Langmuir probes) are of limited utility in depositing plasmas, high pressure applications or in processes that require the use of reactive gases, as these environments result in unreliable data acquisition. Plasma frequency probes are an attractive alternative to Langmuir probes in such applications since they do not suffer significant performance degradation in these environments. This work presents frequency probes measurements of plasma density over a range of 10^9 to 10^{12} cm^{-3} in a variety of processing plasma chemistries (N_2, CH_4, NH_3, O_2 and SF_6). In addition to electron density measurements frequency probes are also useful for measuring plasma potential, electron temperature, and electron energy distribution functions in the gas chemistries mentioned above.

2:40pm PS2-TuA3 Effects of Wire Thickness, Neutral Pressure and Gas Composititon on the Inflection Point Technique, *B. Dechawatanapisal, N. Hershkowitz, J.P. Sheehan, CS. Yip*, University of Wisconsin-Madison

The inflection point technique in the limit of zero emission determines the plasma potential by fitting a straight line to the graph of the emission current versus the inflection point of the emissive probe I-V traces. The plasma potential is determined by extrapolating the line to the limit of zero emission. The effects of wire thickness, gas composition, neutral pressure and position on the technique were investigated. Experiments were performed in a multi-dipole filament discharge. Wire thicknesses of 0.013, 0.025, 0.05 and 0.1mm were studied. Experiments were done in Argon, Xenon and Helium plasmas with neutral pressures ranging from 0.5mTorr

to 3mTorr. Measurements were performed from the bulk of the plasma to its sheath edge near a 10cm diameter negatively biased plate.

3:00pm PS2-TuA4 A New Diagnostic Tool System of Radio-Frequency Plasmas by Employing Floating-Emissive Probe, *Y. Taniuchi, M. Utsumi,* Tokai University, Japan*, M. Yanagisawa,* Landmark Technology Corporation, Japan*, H. Shindo*, Tokai University, Japan
A new diagnostic tool to measure plasma parameters as well as Electron Energy Distribution Function (EEDF) by a floating-emissive probe has been proposed[1], and a diagnostic system has been newly developed and applied to radio-frequency (RF) plasmas. It is generally difficult for a conventional probe method to measure EEDF in RF plasmas, because of the plasma potential fluctuation, particularly in the capacitive mode. The present method has an advantage that there is no need of an external compensation circuit and all measurements can be made in the floating condition. The method is based on measurement of the functional relationship between the floating potential change ΔV_F and the heating voltage V_H of emissive probe. If the plasma electrons are in Maxwellian, the equation can be obtained for the value of ΔV_F as a practical and useful formula.[1]

It is important to know that the value of ΔV_F contains information of electron energy distribution. In the experiment, the data of V_F and ΔV_F was measured in a 13.56 MHz RF plasma produced by single-loop antenna[2], as a function of V_H. In the conditions of high RF power, the plasma mode was ICP and the measured values of ΔV_F were in agreement with the theoretical value, stating that the plasma electron was in Maxwellian. The electron temperatures thus obtained were very consistent with those measured by Langmuir probe. The electron density was also obtained from the value of ΔV_F near the plasma space potential and they were consistent with Langmuir probe data. Consequently, by using a new diagnostic system one can obtain the electron temperature and density, the plasma space potential and floating potential, as well as the EEDF in the floating condition of the probe. It should be stressed that this is the first success of floating probe to be able to measure all plasma parameters. One can also expect that the present method is applied to plasmas which are produced in insulated vessels.

References:

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

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

4:00pm PS2-TuA7 A Comparison of Emissive Probe Techniques for Electric Potential Measurements in a Complex Plasma, *J.P. Sheehan*,* University of Wisconsin-Madison*, Y. Raitses,* Princeton Plasma Physics Laboratory*, N. Hershkowitz,* University of Wisconsin-Madison*, I. Kaganovich, N.J. Fisch*, Princeton Plasma Physics Laboratory
Accurate measurements of the plasma potential is a critical challenge especially for complex plasmas such as magnetized and flowing. We compare various emissive probe techniques for measurements of the plasma potential. The measurements were conducted in a low-pressure magnetized discharge of the Hall thruster. The thruster was operated with xenon gas in subkilowatt power range and the discharge voltage range of 200-450 V. The probe was placed at the channel exit where, the electron temperature is in the range of 10 to 60 eV and the plasma potential is in the range of 50 to 250 V. The floating point method is expected to give a value ~Te/e below the plasma potential. The experimental results are consistent with these expectations. Specifically, it is shown that the floating potential of the emissive probe is ~2Te/e below the plasma potential. It is observed that the separation technique varies wildly and does not give a good measure of the plasma potential.

4:20pm PS2-TuA8 Probe Diagnostics Instrument for Laboratory and Industrial RF Plasmas, *V. Godyak*, RF Plasma Consulting
Contemporary probe diagnostics of low pressure rf discharge non-Maxwellian plasmas implies the measurement of electron energy distribution function, EEDF and variety of plasma parameters found as the

* Coburn & Winters Student Award Finalist

corresponding EEDF's integrals. There are four major problems in implementing of meaningful probe diagnostics in rf plasma reactors. They are: a) large frequency spectrum with significant amplitudes of the plasma rf potential corresponding to source and bias fundamental frequencies and their harmonics; b) low frequency noise due to plasma instability and ripples in an rf power source, c) too high impedance between the plasma and grounded chamber due to limited surface of the chamber and its contamination or/and an artificial protective coating, and d) contamination of the probe surface with a low conductive layer of the reaction products. The probe characteristic distortion caused by these factors are hardly recognized when one just follows Langmuir procedure to infer plasma parameters assuming Maxwellian EEDF, since distorted and undistorted probe characteristics look similarly. But the problem becomes apparent after double differentiation of the distorted probe characteristics (to infer the EEDF) due to error augmentation inherent to differentiation procedure. A probe diagnostic system VGPS® [1], addressing the aforementioned problems has been designed and tested in the variety of rf plasmas in basic research experiment and in different rf plasma reactors. Examples of EEDF measurements with high energy resolution (small fraction of T_e) and large dynamic range (3-4 orders of magnitude) in laboratory and industrial rf plasmas, are given in this presentation.

4:40pm **PS2-TuA9 Ion Energy Distributions in Pulsed Plasmas with Synchronous DC Bias: Effect of Noble Gas**, *W. Zhu*, *H. Shin, V.M. Donnelly, D.J. Economou*, University of Houston
Ion energy distributions (IED) on the substrate electrode were measured in a Faraday-shielded inductively coupled plasma. Narrow distributions with well-controlled ion energy were obtained by pulsing the plasma and applying a synchronous DC bias on a "boundary" electrode during the afterglow. The peak ion energy was controlled by the DC bias, as the plasma potential and the electron temperature decayed drastically in the afterglow. IED measurements were performed in Ar, Kr and Xe plasmas, using a retarding field energy analyzer. A Langmuir probe was also used to measure time- and space-resolved plasma density and electron temperature during a pulse as a function of power and pressure. The quasi-steady electron temperature (late in the active glow) followed the order Ar > Kr > Xe i.e., the gas with the highest ionization potential had the largest electron temperature. The opposite order of T_e (Xe > Kr > Ar) was observed in the afterglow, as the decaying electron temperature was controlled by diffusion cooling, and the diffusivity is lower for heavier gas. The full width at half maximum (FWHM) of the IEDs followed the order Xe>Kr>Ar. Higher electron temperature in the afterglow correlated with larger FWHM. The width of the IED could also be controlled by varying the pulsed plasma frequency and duty cycle, or the time window of the application of the DC bias during the afterglow. Small additions (up to 5% by volume) of chlorine gas resulted in IEDs that were similar to those in the corresponding pure noble gas plasma, except that the peak ion energy was lower by a few eV.

5:00pm **PS2-TuA10 2011 AVS John A. Thornton Award Lecture - As Device Dimensions Continue to Shrink… A Journey Through Thirty Years of Plasma Etching Diagnostics and Mechanisms**, *V.M. Donnelly**, University of Houston   **INVITED**
With each new generation of integrated circuits and reduction in transistor and interconnect dimensions, plasma etching of fine features in silicon, aluminum and insulating thin films encounters new sets of challenges. Over the past thirty years, our understanding and control of plasma etching processes has greatly improved, due to the advances in diagnostic techniques and basic mechanistic studies, combined with advanced modeling methods. This talk will review studies, mostly from our laboratories, spanning this era with an emphasis on the connections between studies, the influence of other fields, and the interactions between collaborators and colleagues. Some old controversies will be revisited and perhaps revived.

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* John A. Thornton Memorial Award Winner

Plasma Science and Technology Division
Room: 201 - Session PS+SE-WeM

Atmospheric Plasma Processing and Micro Plasmas
Moderator: P.L.S. Thamban, University of Texas at Dallas

8:00am **PS+SE-WeM1 2011 AVS Peter Mark Award Lecture - Microscale, Atmospheric-Pressure Plasmas: A Platform for Nanomaterials Synthesis at Different Length Scales**, *M. Sankaran**, Case Western Reserve University **INVITED**
Large-scale, low-pressure plasmas play an essential role in the processing of materials for a wide-range of applications including integrated-circuit (IC) manufacturing. In recent years, new challenges have arisen for these top-down approaches to materials processing. Advanced electronic devices will be comprised of nanomaterials such as nanoparticles and carbon nanotubes that cannot be fabricated by current plasma technology because of limitations associated with photolithography. In addition, emerging applications in sensors, energy, and medicine require nanomaterials that must be prepared from the "bottom-up" and assembled into macroscale structures. The aim of our research is to develop a new class of plasmas, termed microplasmas, for nanomaterials synthesis and assembly.

Microplasmas are electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their pD scaling (p is the gas pressure and D is the smallest dimension), microplasmas operate stably at atmospheric pressure. These properties open up unique opportunities for nanomaterials synthesis and assembly. For example, vapor-phase metal-organic precursors can be dissociated near ambient conditions to homogeneously nucleate metal [1] and alloyed [2] nanoparticles. The formation of well-defined metal nanoparticles in the gas phase allows direct introduction of these materials as catalysts for chiral-enriched carbon nanotube growth [3]. Recently, we have also coupled microplasmas with liquids to electrochemically synthesize nanoparticles from aqueous metal salts [4]. By extending this strategy to thin films, microscale patterns of nanoparticles are fabricated in a single step [5]. In this talk, I will discuss these topics in detail, highlightingthe advantages of microplasma-based systems for the synthesis of well-defined nanomaterials at various length scales.

1. W-H. Chiang and R. M. Sankaran, Appl. Phys. Lett. **91**, 121503 (2007).

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3. W-H. Chiang and R. M. Sankaran, Nat. Mater. , 882 (2009) .

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S. W. Lee, D. Liang, X. P. A. Gao, and R. M. Sankaran, Adv. Func. Mater., available online: doi: 10.1002/adfm.201100093.

8:40am **PS+SE-WeM3 Surface and In-Depth Modification of LDPE using an Atmospheric Plasma Torch**, *S. Abou Rich, P. Leroy,* Universite Libre de Bruxelles, Belgium, *N. Wehbe,* Universiy of Namur, Belgium, *N. Avril, L. Houssiau,* University of Namur, Belgium, *F. Reniers*, Universite Libre de Bruxelles, Belgium
In order to improve the adherence of a coating onto a polymer, the substrate surface must be properly functionalized. Plasma techniques are more and more used for that purpose. However, plasma treatments do not only modify the polymer surface, as active species can penetrate into its bulk.

In the present study, polyethylene samples are surface-functionalized by an atmospheric plasma torch, using argon and a mixture of argon-oxygen. The surface is characterized by dynamic water contact angle, atomic force microscopy and X-ray photoelectron spectroscopy. The changes in the bulk of the polymer have been characterized using infrared spectrometry, angle-resolved X-ray photoelectron spectroscopy (ARXPS), and secondary ion mass spectrometry (SIMS).

It is shown that both plasma treatments (argon or argon-oxygen) lead to an increase in the hydrophilicity of the surface by the grafting of oxygen-containing polar functions. AFM reveals also a change in surface roughness induced by the plasma treatment, depending on the operational conditions. FTIR, ARXPS and SIMS evidenced that the plasma treatment also modifies a significant zone under the surface. The diffusion depth of oxygen as a function of the plasma parameters (power, treatment time, oxygen ratio in the gas phase) is determined.

The ageing of the plasma-modified polymers during storage in air is also studied

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* Peter Mark Memorial Award Winner

9:00am **PS+SE-WeM4 Surface Analysis of Polymers Treated by Remote Atmospheric Pressure Plasma**, *R.F. Hicks*, University of California Los Angeles, *E. Gonzalez,* Intel Corporation, *T.S. Williams*, University of California Los Angeles
Atmospheric plasma treatment is a key process for improving the adhesive bond strength of polymers in many products, such as thermoplastic composites on jet aircraft and helicopters, molded plastic parts in automobiles, and plastic tubing and stents in implantable medical devices. In this study, the surfaces of high-density polyethylene (HDPE), poly(methyl methacrylate) (PMMA), and polyethersulfone (PES) were treated with a low-temperature, atmospheric pressure oxygen and helium plasma. The polymers were exposed to the downstream afterglow of the plasma, which contained primarily oxygen atoms and metastable oxygen molecules ($^1\Delta_g$ O_2), and no ions or electrons. X-ray photoelectron spectroscopy of HDPE revealed that 20% of the carbon atoms were converted into oxidized functional groups, with about half of these being carboxylic acids. Attenuated total reflection infrared spectroscopy of all three polymers was obtained in order to determine the types of functional groups formed by atmospheric plasma exposure. It was found that the polymers were rapidly oxidized with addition of alcohols, ketones, and carboxylic acids to the carbon backbone. Chain scission occurred on HDPE and PMMA, while on PES the aromatic groups underwent ring-opening and insertion of carboxylic acid. The implications of this work for forming strong adhesive bonds to these polymers will be discussed at the meeting.

9:20am **PS+SE-WeM5 Deposition of SiO$_x$ Films by Means of Atmospheric Pressure Microplasma Jets: Study of Deposition Mechanism**, *J. Benedikt*, R. Reuter, D. Ellerweg, K. Ruegner, T. de los Arcos, A. von Keudell, Ruhr-University Bochum, Germany **INVITED**
Deposition of thin films with plasmas at atmospheric pressure is always a challenging task because of high collision rates, absence of ion bombardment, filamentary behavior of the plasma and limited knowledge of plasma chemistry. The preparation of high quality thin films is therefore still the main domain of low pressure plasmas. One of films, which can be prepared at atmospheric pressure, is SiO$_2$. Hexamethyldisiloxane (HMDSO) and O$_2$ (or N$_2$O) are usually used as precursors fed into the plasma.

We have shown in the past that a good quality SiO$_2$ films can be prepared by means of microplasma jets driven by RF voltage and operated in Ar or He as plasma forming gas. Here we concentrate on the study of plasma chemistry and surface reactions leading to the film growth. The geometry of the microplasma jet and the localization of the plasma treatment allow studying of gas phase reactions and plasma-surface interaction separately. Molecular beam mass-spectrometry is used to measure HMDSO depletion and stable products in the gas phase. Depletion below 15% and limited fragmentation is observed even under conditions with high O$_2$ density, which leads to formation of carbon free SiO$_2$ films. The plasma-surface interaction is studied by application of several jets with different gas mixtures (He/HMDSO, He/O$_2$, He/H$_2$...) to the same trace on the rotating substrate in controlled helium atmosphere. It is shown that surface reactions are responsible for the carbon removal from the grown film. Infrared spectroscopy, spectroscopic ellipsometry and X-ray photoelectron spectroscopy measurements are performed to analyze film properties and compare them with plasma measurements. A fluid model of gas flow and reaction kinetics in the effluent of the plasma is used to reproduce observed trends and measured deposition rates. Good agreement is achieved with relatively simple model of plasma chemistry and surface reactions.

11:00am **PS+SE-WeM10 Synthesis of Li$_4$Ti$_5$O$_{12}$ Nanoparticles Using an Atmospheric Plasma Jet**, *S.M. Chang*, E.F. Rodriguez, H.C. Li, Y.J. Yang, N.L. Wu, C.C. Hsu, National Taiwan University, Taiwan, Republic of China
Nanocrystalline spinel Li$_4$Ti$_5$O$_{12}$ (LTO) is a promising anode material for Li-ion batteries due to its zero-strain during intercalation/deintercalation and the 1.5 V (vs. Li+/Li) potential plateau. Development of a process that allows for rapid synthesis with controllable microstructure has been challenging. In this work, LTO nanocrystalline particles synthesized by an atmospheric pressure plasma jet (APPJ) will be presented. The APPJ is sustained using a repetitive pulsed power source with N$_2$ gas. Ti and Li ions-containing solution of specific formula is used as the precursor solution. The precursor is ultrasonically nebulized and is then carried into the downstream of the APPJ using a carrier gas. With this process, nanocrystalline LTO can be fabricated in one step with a short contact time (a few ms) between the precursor and the plasma jet without an additional annealing process. The LTO particle size can be effectively controlled using the precursor solution concentration and the carrier gas flow rate. 100-300 nm dense spherical particles can be fabricated under an optimized

condition. The microstructure and porosity of the particles is strongly influenced by the pre-heat process for the nebulized precursor droplets prior to entering the jet downstream. Dense spherical and porous particles are fabricated under conditions with and without preheating, respectively. Finally, full battery performance test will be presented and key factors that dominate the fabricated nanoparticle characteristics will be discussed.

11:20am PS+SE-WeM11 Laser-Assisted Plasma Coating at Atmospheric Pressure: Production of Yttria-Stabilized Zirconia Thermal Barriers, *Z. Ouyang*, *P. Raman, Y.L. Wu, L. Meng, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana-Champaign
A laser-assisted plasma-coating technique at atmospheric pressure (LAPCAP) for use in thermal-barrier coatings (TBC) deposition has been developed. This technique allows PVD-quality depositions to be done at atmospheric pressure. The microwave source employed has a working frequency at 2.45 GHz, and a maximum input power of 6 kW, and the attached plasma torch head has the ability to generate various types of atmospheric-pressure plasmas at the temperatures of room temperature (20°C) to more than 2,000 °C. Optical emission spectroscopy (OES) technique has been used to spatially analyze some critical characteristics of plasma, such as electron density ($n_e > 10^{14} cm^{-3}$), electron temperature ($T_e \sim$ 1 eV), and plasma gas temperature ($T_g \sim$ 400-3,000 K), under different operating conditions (gas type, input power and gas flow rate). A helium atmospheric plasma has been used to assist in Nd:YAG laser ablation (f = 100 Hz, Energy/pulse = 20 mJ at 266 nm; 120 mJ at 532 nm; 325 mJ at 1064 nm) of a 3% yttria-stabilized zirconia (3YSZ) target, to provide a means to deposit high quality, adhesive thin films on René N5 superalloy substrates with better lamination at a relatively higher deposition rate (~1,000 nm/min), in comparison to traditional PVD methods. The morphology and characteristics of the films have been compared at three laser wavelengths (266 nm, 532 nm and 1064 nm), different laser energy densities (1-10 J/cm^2) and substrate temperatures (20-1100 ℃), using microanalysis techniques such as scanning electron microscope (SEM), focused ion beam (FIB), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

11:40am PS+SE-WeM12 Investigation on the Discharge Formation Mechanisms and Surface Analysis of SiO$_2$-like Layers on Polymers Synthesized using High Current Dielectric Barrier Discharge at Atmospheric Pressure, *M.C.M. van de Sanden*, FOM-Inst. for Plasma Phys. Rijnhuizen & Eindhoven Univ. of Tech., Netherlands, *A. Premkubar*, Eindhoven Univ. of Tech. & M2i, Netherlands, *S. Starostin, H. de Vries*, Fujifilm Tilburg, Netherlands, *M. Creatore*, Eindhoven Univ. of Tech., Netherlands
The dielectric barrier discharge is recognized as a promising tool for PECVD of thin films at atmospheric pressure. Emerging applications including encapsulation of flexible solar cells and flexible displays requires low costs production of transparent uniform and dense layers with low level of coating defects. Among the two discharges Townsend like discharge (TD) and glow like discharge (GD) the latter offers more flexibility for the high growth rates in plasma enhanced deposition. In this investigation we demonstrate the utilization of glow like discharge in, He free, industrially relevant gas mixture comprising Ar/N$_2$/O$_2$/HMDSO for the deposition of high quality silica like films on large area polymeric substrates (PET or PEN) in a roll-to-roll configuration. While the discharge physics exhibiting the glow like behaviour is investigated via fast ICCD camera, voltage-current waveforms and optical emission spectroscopy, the deposited silica like films is comprehensively analyzed using AFM, SEM, XPS, SE and FTIR. The time evolution of the diffuse atmospheric discharge showed several phases starting from the initial ignition of the low current Townsend-like mode followed by the transition to glow like discharge which then undergoes lateral expansion providing uniform treatment of the whole substrate width. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N$_2$ or air) employed, the films are smooth, both locally and globally, and of near stoichiometric silica with very low carbon content (< 2%). Detailed AFM morphology description and surface statistical analysis on SiO$_2$ dynamics showed that no film roughening in growth front and lateral directions observed and the synthesized layers (~ 350 nm) grow in a self-similar fashion following the topology of the substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O$_2$ and H$_2$O permeation.

Plasma Science and Technology Division
Room: 202 - Session PS+SS-WeM

Plasma Surface Interactions (Fundamentals & Applications) I
Moderator: C. Labelle, GLOBALFOUNDRIES

8:00am PS+SS-WeM1 Investigation of Sidewall Passivation Mechanism in a 'CMOS-compatible' Plasma Etching Process for InP-based Photonic Devices, *S. Bouchoule*, CNRS-LPN, France, *L. Vallier*, CNRS-LTM, France, *L. Gatilova, G. Patriarche, S. Guilet, L. Le Gratiet*, CNRS-LPN, France
Inductively coupled plasma (ICP) etching of II-V semiconductors is now widely used for the development of high-performance emitters, and various chlorine- or HBr- containing chemistries have been proposed for the patterning of InP-based heterostructures required to reach the NIR region. Smooth and anisotropic etching is generally a key-requirement, but only few studies exist on the understanding of the sidewall passivation mechanisms occurring during the etching of InP and related materials. We have shown for the Cl$_2$-H$_2$ and HBr chemistries [JVSTB 26, 666 (2008)] that a silicon oxide layer acting as a lateral etch-inhibitor can build-up on the etched sidewalls of InP-based heterostructures, when a Si wafer is used as the sample tray. This configuration corresponds to most commercial ICP etch systems having an electrode diameter of 4-in or more, used to etch III-V samples of 2-in or less size. However, this may not be the case for future large surface processing of III-V when the III-V wafer will have the same size as the electrode or when III-V dies bonded onto a 200/300 mm wafer have to be etched, where most of the wafer surface is covered by a protecting layer that is not silicon. This may occur in III-V/Si photonic technologies. We have shown that high-aspect- ratio etching of the photonic patterns via a SiO$_x$ sidewall passivation mechanism independent of the electrode surface can be obtained when a Si-containing gas such as SiH$_4$, or SiCl$_4$ added [JVSTB 29, 020601 (2011)]. A more detailed analysis of the plasma has shown that hydrogen may promote the deposition of a Si-rich passivation layer on the sidewalls of the etched patterns. SiOCl sidewall passivation takes place during Si ICP etching using Cl$_2$-HBr-O$_2$ chemistry in CMOS technology. We have therefore investigated SiCl$_4$/Cl$_2$/HBr/O$_2$/Ar plasma for the etching of InP dies in a 300-mm CMOS etching tool. This gas mixture provides the Si,O, and H species required for the build-up of a SiO$_x$ passivation layer on the InP sidewalls. We show that the passivation mechanism is enhanced when the HBr concentration is increased in the feed gas. We have performed a local analysis of the passivation layer deposited on the InP sidewalls using EDX spectroscopy coupled to TEM. We show that the nature of the passivation layer can be changed from a-Si or nc-Si to SiO$_2$ depending on the hydrogen and oxygen concentrations in the gas mixture. Finally we demonstrate smooth and anisotropic etching of ridge waveguide and vertical Bragg reflector patterns in the CMOS etching tool.

8:20am PS+SS-WeM2 Coupling of Surface Mixed-Layer Kinetics and Monte Carlo Modeling for Profile Evolution in Patterning Complex Oxides, *N. Marchack*, C.D. Pham, J.P. Chang*, University of California Los Angeles
As the downscaling of integrated circuit devices continues, minute variations in the feature profiles from processing techniques such as plasma etching significantly affect device performance. With the increasing introduction of novel materials into integrated circuits, the need to predict surface response during etching of these materials, such as complex oxides, becomes critical to attainable device performance. In this work, a phenomenological model[1] based on high-k oxide etching in chlorine based plasmas is adapted into a translated mixed layer (TML)[2] kinetics-based format to be used a Monte Carlo-based feature profile simulator. To accurately represent the kinetics involved, experiments are conducted in this work in an inductively coupled plasma (ICP) reactor equipped with a quadrupole mass spectrometer (QMS) for analyzing etch products and a quartz crystal microbalance (QCM) for measuring the etch rate *in situ*. This reactor is connected to a UHV transfer tube which allows the surface composition to be studied via x-ray photoelectron spectroscopy (XPS) without exposure to ambient conditions. In the TML model, surface reactions such as ion impingement, neutral adsorption, physical sputtering and chemically enhanced ion etching are accounted for, and reaction parameters are either measured directly or extracted by comparing the model to etch yield data. The MC model used ion incident angle dependence and an elliptical energy deposition model to capture the effects of surface morphology on the profile evolution under the bombardment of energetic and directional ions. The material systems studied include HfLaO

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* Coburn & Winters Student Award Finalist

and HfSiON etched in Cl_2/BCl_3 plasmas, for both blanket films and trenches patterned by e-beam lithography. Very good agreement was demonstrated between the phenomenological and TML models, as well as between simulated profiles and cross-sectional SEM images of the patterned material systems.

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

[2] Kwon et al. Journal of Vacuum Science and Technology A. 24(5) 2006

8:40am PS+SS-WeM3 Plasma Diagnostics and Nanoscale Surface Processing - Application to SiO₂, High-k PVD and ALD, *T. Kitajima*, National Defense Academy, Japan **INVITED**

Introduction

Reactive plasmas are widely used for surface processings due to its controllable ion energy and radial fluxes.

Nano size feature control with plasma processing requires nonthermal chemistry with low energy ion exposure. Metastable atoms with internal energy of a few eV become important for the quality and throughput of deposition as ion energy is reduced.

Minimizing the processing target to the nanoscale also reveals the new properties of materials interacting with plasmas due to the size effect. Namely, sticking coefficients of radicals on metal significantly increase.

In the presentation, some recent results on metastable radical induced deposition including HfO2 ALD are shown. The latest findings of nano particle interaction with reactive plasmas are introduced for the model case of PVD based HfSiON film growth.

Reactive metastables for oxide growth : SiO2 and HfO2

The density of metastable O(1D) (1.9eV) in Ar-diluted O2 ICP shows maximum at O2 fraction of 1% and the flux shows significant increase due to the reduced quenching by O2. O(1D) density is measured by Vacuum UltraViolet Absorption Spectroscopy (VUVAS). The XPS analysis shows the stoichiometry of the grown SiO2 is comparable to the thermal oxide as well as the electrical breakdown.

The scheme is applied to the plasma enhanced atomic layer deposition (PEALD) of HfO2. The reagent is TEMAH and the oxidant is Ar-diluted O2 ICP. The increased O(1D) flux enables less particle film surface with fewer carbon contamination.

Reactive surface nano particles interacting with plasma : HfSiON growth

Hf nanoparticles self assembled on SiO2/Si(100), origin of HfSiON, have sticking coefficient of N radicals close to 1 in the initial stage of N2 ICP exposure. The reactivity of the nanoparticles with underlying SiO2 is enhanced by the plasma exposure, results in the formation of carbon free HfSiON film.

Concluding remarks

Metastables are important reactant for low temperature non-biased deposition processes

Metastable flux is controllable with the base gas chemistry

Nanoscale surface features are current concerns for plasma deposition

Nano sized surface has totally different reaction kinetics including interface with underlayer

Nano size effect of the surface is evident for radical reactivity

Self assembly (bottom up scheme) is highly important for next generation nano scale plasma processing as well as lithographic techniques (top down scheme)

Acknowledgement

9:20am PS+SS-WeM5 Nitric Oxide Reactivity Investigation via Plasma Processing, *J.M. Blechle*, *E.R. Fisher*, Colorado State University

With increasing concern about environmental health, there is a greater need to investigate fundamental reactivity of pollutant species with and without the influence of surface effects. Here, inductively coupled plasmas are used to examine the catalyzed conversion of industrial exhaust, with an emphasis on elucidating the surface and gas-phase chemistry. Literature studies have thus far failed to explore the primary driving forces present in these catalytic plasma systems. The present work focuses on investigating the properties of nitric acid within plasmas formed from a collection of precursor gases including NO, NO_2, N_2O, and N_2+O_2. The behavior of the NO radical is determined by various methods that include catalytic surface reactivity measurements via the imaging of radicals interacting with surfaces (IRIS) technique as well as kinetic formation and destruction via time-resolved optical emission spectroscopy (TR-OES). Species density,

surface scatter coefficients (*S*), along with vibrational and rotational temperatures establish inherent characteristics of NO. Results from these studies show the density of NO is strongly dependent on system pressure, which is in part attributable to formation of gas-phase dimers. In addition, *S*(NO) using non-catalytic surfaces (e.g. Si) increases with increasing plasma power. Additional results from studies of NO formation through bimolecular reactions in N_2/O_2 plasmas will be presented. Collectively, these data allow for unparalleled insight into the properties of atmospheric species during plasma processing and the interactions they undergo in the presence of catalytic substrates.

9:40am PS+SS-WeM6 Near-Threshold Ion-Enhanced Silicon Etching, *H. Shin*, *W. Zhu, V.M. Donnelly, D.J. Economou*, University of Houston

Nearly mono-energetic ion energy distributions (IED) were obtained on the substrate electrode in a Faraday-shielded inductively couple plasma. This was accomplished by pulsing the plasma, and applying a synchronous DC bias on a "boundary" electrode, during a specified time window in the afterglow. Both the peak ion energy and the width of the IED could be controlled.[1] The ability to precisely control the IED enabled a study of ion-enhanced etching of silicon with chlorine, at near-threshold ion energy. Unlike "beam" experiments, where there is no plasma over the substrate, this work involves etching under "realistic" plasma conditions. The progress of etching in an argon-diluted chlorine plasma was monitored as a function of pressure and ion energy using optical emission spectroscopy. The silicon etch rate was measured using infrared laser interferometry. The etch rate of a p-type blanket silicon substrate was proportional to Cl-atom density, but did not depend on ion energy for sub-threshold (less than ~ 20 eV) ions. Under these conditions, however, the etch rate was much higher than that expected based on reported experiments in downstream plasmas where the surface is exposed to Cl atoms alone. Above threshold, the etch rate increased with the square root of ion energy. A comparison with n-type silicon substrate was also made. The carrier-mediated mechanisms of p-type Si etching in a plasma under very low energy ion bombardment will be proposed and discussed.

[1] H. Shin et al., to appear in *Plasma Sources Science and Technology.*

10:40am PS+SS-WeM9 Atomic Chlorine Absolute Densities and Surface Recombination Coefficients in Inductively-Coupled Plasmas in Pure Cl₂, *J.-P. Booth*, LPP-CNRS, France, *N. Sirse*, NCPST Dublin City University, Ireland, *Y. Azamoum, P. Chabert*, LPP-CNRS, France

Two-photon laser-induced fluorescence (TALIF) at 233.2nm was used to measure the density of Cl atoms in a 13.56MHz Inductively-coupled plasma in pure chlorine. Initial attempts to use the technique proposed by Ono et al [1], to calibrate the signal using photolysis of CCl4 gave unphysically high values, probably due to poor knowledge of the laser spatial profile at the focal point. Therefore we developed a new technique, based on 355nm (tripled YAG) photolysis of Cl2 to generate a known density of Cl atoms. The variation of the absolute Cl density at the reactor centre was measured as a function of pressure and RF power in the range 3-90 mTorr and 20-500W. We also used the TALIF technique to determine the recombination coefficient, γ_{Cl}, of atomic chlorine at the reactor walls from the rate of decay of the Cl density in the afterglow of a pulsed discharge. The signal to noise ratio is good enough to make measurements far into the afterglow (50 ms), when the gas has cooled to the wall temperature, making a precise measurements possible. We found that γ_{Cl} varies in the range 0.05-0.15, decreasing with increased pressure and RF power, and increasing with gas residence time. We show that the latter effect is due to the increased proportion of O_2 due to inevitable small air leaks: the presence of 0.5% O2 was shown to double the value of γ_{Cl}. The origin of the pressure and power dependencies will be discussed.

[1] K. Ono, T. Oomori, M. Tuda, and K. Namba, Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, **10**, 1071, (1992).

11:00am PS+SS-WeM10 Silicon Etching Characteristics by Hydrogen Halide Ions (HCl⁺ and HBr⁺) and Ions of Desorbed Species (SiClx⁺), *T. Ito*, *K. Karahashi*, Osaka University, Japan, *S.-Y. Kang*, Tokyo Electron Ltd., Japan, *S. Hamaguchi*, Osaka University, Japan

In recent reactive ion etching (RIE) processes for Si, halogen and hydrogen halide gases, such as Cl_2 and HBr, have been widely used to achieve high selectivity, etching anisotropy, and high etching rates. Furthermore, in some highly selective silicon etching processes, higher gas-pressure processes have been found to be more effective. In higher-pressure systems, chemical compounds formed from the input gas and some of desorbed species containing Si may serve as additional etchants. To develop etching equipments based on such plasma chemistry, it is important to understand

basic etching reactions on silicon surfaces by energetic ion species associated with silicon and/or hydrogen containing species. To clarify the roles of SiClx, SiBrx, HCl, and HBr in silicon etching processes, we have employed a mass-analyzed ion beam system that can irradiate a sample surface with a specific ionic species under an ultra-high vacuum condition and evaluated the etching yields. The change in chemical nature of the substrate surface during the process can be observed in situ by X-ray photoelectron spectroscopy (XPS) installed in the reaction chamber. Time of Flight (TOF) measurement of species desorbed from the sample surface in a pulsed ion beam operation is also possible with the use of a differentially pumped quadrupole mass spectrometer (QMS). In this study, etching yields of silicon by Cl^+, $SiCl^+$, $SiCl_3^+$, Br^+, H^+, HCl^+, and HBr^+ ion beams were evaluated with incident energies of 100 – 1000 eV. A typical ion dose for each ion irradiation was 2– 4E17/cm2. Yields by some of these ionic species have been known and our etching yield data are confirmed to be in good agreement with the earlier data. It is found that, for a given incident energy, the etching yield by $SiCl_3^+$ ions is higher than that by Cl^+ ions whereas the etching yield by $SiCl^+$ ions is lower than that of Cl^+ ions, which may be accounted for by the number of Cl atoms and a possible deposition effect of Si. It has been also observed that deposition occurs under $SiCl^+$ ion irradiation when the injection energy is lower than 300eV. Energy dependence of etching yields and effects of hydrogen will be discussed in detail.

11:20am **PS+SS-WeM11 Interaction of Chlorine Plasma with Si_xCl_y Coated Plasma Reactor Chamber Walls**, *R. Khare*, A. Srivastava, V.M. Donnelly*, University of Houston

The interplay between chlorine plasmas and silicon chloride (Si_xCl_y) coated reactor walls has been studied by line-of-sight mass spectrometry in a radio frequency (rf) inductively coupled Cl_2 plasma (ICP), using the spinning wall method. A bare silicon wafer was etched in a 400 Watt Cl_2 ICP, with rf power applied to the stage resulting in a -110 VDC self-bias. Etch products were deposited on the plasma reactor walls and the rotating substrate surface, resulting in a thick layer of Si_xCl_y that was characterized *in situ* by Auger electron spectroscopy. Some oxygen also incorporated into the film due to erosion of the fused silica discharge tube. The reactions of chlorine plasmas with this prepared surface were then studied by line-of-sight mass spectrometry. Without substrate bias, the chlorine plasma etches the Si_xCl_y layer to form products that result in detection of $SiCl_x$ (x = 1-4) m/e components, as well as oxy-silicon-chloride products (m/e= 177, 247, 307, 361). In one experiment, after the deposition of dense Si_xCl_y layer on reactor and substrate surfaces, substrate rotation was stopped and the film was etched from the reactor walls with the chlorine plasma, leaving only the Si_xCl_y layer on 2/3rd of the substrate surface that was out of the plasma. Upon resuming rotation, and exposing the Si_xCl_y loaded surface to the Cl_2 plasma, $SiCl_x$ products were detected, but at suppressed levels, indicating that the evolution of etch products is a complex "recycling" process in which these species deposit and desorbs from the walls many times, and repeatedly fragment in the plasma. These and other experiments will be discussed. This work is supported by the National Science Foundation and Lam Research Corporation.

11:40am **PS+SS-WeM12 Numerical Simulation of Enhanced Oxygen Diffusion in Silicon as a Cause of Si Recess**, *K. Mizotani, M. Isobe,* Osaka University, Japan*, M. Fukasawa, T. Tatsumi,* Sony Corporation, Japan*, S. Hamaguchi*, Osaka University, Japan

In a gate etching process, the formation of hollowed Si profiles around the polysilicon (poly-Si) gates, which is now widely known as "Si recess," has raised serious concern in the semiconductor processing community as such hollows on a Si surface can severely degrade the device performance and reliability. In a typical process that causes Si recess, a plasma based on HBr and oxygen gases are used to etch polysilicon gates anisotropically. A recent study [1] based on multiple-beam and plasma experiments has shown that Si recess is caused by ion assisted oxygen diffusion, i.e., oxygen diffusion enhanced by hydrogen ion injections. In this study, we have used molecular dynamics (MD) simulations to understand the mechanism of enhanced oxygen diffusion in Si under such conditions. In the simulations, energetic hydrogen ions and low-energy oxygen atoms (with kinetic energies close to room temperature) are simultaneously injected into a crystalline Si substrate initially covered with a native oxide layer. Simulation results are in good agreement with ion beam experiments performed under similar conditions given in Ref. [1]. In our simulations, O atoms are transported into the bulk Si due to momentum transfer from energetic hydrogen ions. In other words, the enhanced ion transport is not typical "diffusion" associated with thermal motion in solid. However, random walk characteristics of O atoms in Si under such conditions are interestingly similar to those of diffusion. In this study, we relate this

oxygen transport to diffusion transport and present its effective diffusion coefficient as a function of hydrogen ion injection energy.

[1] T. Ito, K. Karahashi, M. Fukasawa, T. Tatsumi and S. Hamaguchi, "Si recess of Poly-Si Gate Etching: Damage Enhanced by Ion Assisted Oxygen Diffusion," Jpn. J. Appl. Phys. (2011) *in press*.

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* Coburn & Winters Student Award Finalist

Wednesday Afternoon, November 2, 2011

Plasma Science and Technology Division
Room: 202 - Session PS+EM-WeA

Low-K Materials & Integration
Moderator: S. King, Intel Corporation

2:00pm **PS+EM-WeA1** **Electric and Optical Characterization of Leakage and Breakdown in Low-k Dielectric Materials**, *J.M. Atkin, R. Laibowitz*, Columbia University, *T.M. Shaw*, IBM T.J. Watson Research Center, *T.F. Heinz*, Columbia University **INVITED**

Low-k dielectric thin films are finding increased use in integrated circuits for the faster signal speed that they permit. These materials, however, have higher leakage currents and shorter lifetimes than SiO_2–based dielectrics. With the continued push to lower values of k, these problems are becoming more acute.

In this paper, we present results of several complementary characterization techniques for determining key physical properties, such as trap densities and barrier heights, that influence leakage and time-dependent dielectric breakdown (TBBD) phenomena. Electrical characterization techniques include impedance spectroscopy and the measurements of transient currents. In addition, we make use of distinctive optical characterization techniques to obtain specific information about the underlying material properties. Internal photoemission (or photocurrent) spectroscopy yields information on interfacial barrier heights from the photon energies required to induce a current. Optical second-harmonic generation (SHG) provides a sensitive, non-contact method for measuring both photo-driven and spontaneous charge transport. From these methods, we show that the increase in current with long time biasing, which is in turn a precursor to electrical breakdown, can be directly correlated with increased trap densities. Conduction models accounting for the early failure mechanism will be discussed. Partial support for this work from the Semiconductor Research Corporation is gratefully acknowledged

2:40pm **PS+EM-WeA3** **Electron Spin Resonance Study of Low-K Dielectrics and Etch Stop Layers**, *B.C. Bittel*, P.M. Lenahan, T.A. Pomorski, Penn State University, *S. King*, Intel Corporation

The electronic properties of thin film low-κ interlayer dielectric (ILD) and etch stop layers (ESL) are important issues in ULSI development. However as the semiconductor industry looks to transition to 16 nm and beyond technology nodes, numerous concerns with low-κ materials need to be addressed. Leakage currents, time dependent dielectric breakdown and stress induced leakage currents are critical problems that are not yet well understood in ILD. A topic of current interest is ultraviolet light (UV curing) of low-κ materials.

We have made electron spin resonance (ESR) and current density versus voltage measurements on a moderately extensive set (over 50 films) of dielectric/silicon structures involving materials of importance to low-κ interconnect systems. Most of the dielectrics studied involve various compositions of SiOC:H. In addition we have also made measurements on other dielectrics including SiO_2, SiCN:H and SiN:H, some of which are utilized as ESLs. In our study we have made ESR and current density versus voltage measurements both before and after exposing the dielectrics to UV light (hc/λ ≤ 5 eV), and films that have experienced an industrial UV curing process. We observe extremely gross differences in the ESR spectra and leakage current versus voltage response of these low-k films. We find that UV exposure consistently increases both the density of paramagnetic defects and the leakage current density at a given field. Paramagnetic point defects observed in these films include, E' centers, silicon dangling bond defects in which the silicon is back bonded to oxygen, the 74 gauss doublet which is E' center complexed to a hydrogen atom, the 10.4 gauss doublet which is a hydrogen coupled E' center, the K-center which are silicon vacancies back bonded to three nitrogens, and possibly silicon and carbon dangling bond centers and likely organic radicals. We have also made electrically detected magnetic resonance (EDMR) spin dependent trap assisted tunneling measurements on some ILD films. The close correspondence between the ESR and SDT result establishes a direct link between the defects observed in ESR and the defects responsible for the increased tunneling currents. We have also observed a correspondence between ESR amplitudes and leakage currents. Our preliminary results suggest the UV curing process creates paramagnetic centers which take part in trap assisted tunneling. Our results indicate quite clearly that the processing parameters have extremely gross effects upon defect densities within these films.

4:00pm **PS+EM-WeA7** **The Nature of Defects in Low-*k* Organosilicate Glass and their Response to Plasma Exposure**, *H. Ren*, M.T. Nichols, University of Wisconsin-Madison, *G. Jiang, G.A. Antonelli*, Novellus Systems, *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Defect concentrations in low-*k* organosilicate glass [SiCOH] films deposited on high-resistivity silicon were measured with electron-spin resonance. Both plasma exposure and ultraviolet exposure were used. During argon electron-cyclotron resonance plasma exposure, ion and photon bombardment increased the measured defect concentrations. Ultraviolet lamp exposure was also shown to increase the defect concentrations. SiCOH samples with several dielectric constants were examined showing that as the value of the dielectric constant was lowered, the defect concentrations were shown to increase significantly.[i] In addition, the nature of the defects in SiCOH was investigated using air and nitrogen plasma exposure. The defects were found to be silicon dangling bonds. Air-plasma exposure increases the defect concentrations by breaking silicon-hydrogen bonds, measured by Fourier-transform infrared spectroscopy. Nitrogen-plasma exposure as well as free-radical exposure have only a small influence on the bond breaking. It was also shown that UV curing improves the chemical-damage resistance of the dielectric.

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[i] H. Ren, M. T. Nichols, G. Jiang, G. A. Antonelli, Y. Nishi, and J.L. Shohet, *Applied Physics Letters* **98**, 102903 (2011).

4:20pm **PS+EM-WeA8** **The Effects of Plasma Exposure on the Time Dependent Dielectric Breakdown of Low-k Porous Organosilicate Glass**, *M.T. Nichols*, H. Sinha, University of Wisconsin-Madison, *G.A. Antonelli*, Novellus Systems, Inc., *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Time dependent dielectric breakdown (TDDB) is a major concern for newly emerging low-*k* organosilicate (SiCOH) dielectrics. TDDB degradation can be caused by changes in electrical, chemical, and mechanical properties of the dielectric materials.[i] [ii] [iii] [iv] In order to examine the effect of plasma exposure on TDDB degradation, time-to-breakdown measurements were made on porous SiCOH before and after exposure to a variety of plasma exposure conditions. Plasma parameters were changed between exposures such that each sample was subjected to different charged particle and vacuum ultraviolet photon fluxes in order to determine how TDDB degradation was affected by each of them during plasma exposure. By utilizing a capillary-array window to separate charged particle and photon bombardment, it is possible to show that each process is responsible for causing different types of TDDB degradation.

A constant voltage TDDB measurement technique was implemented to analyze unexposed, VUV-irradiated and plasma (charged-particle and photon bombardment) exposed samples to examine the degradation in TDDB. It was observed that the time to breakdown reduces as the electric field stress in increased, which is consistent with what has been previously predicted. It was also found that the unexposed samples exhibit longer time-to-breakdown, indicating highest reliability. Capillary-array-window covered samples exhibited marked degradation in leakage currents and time-to-breakdown relative to the unexposed samples. However, samples exposed to both charged particle and VUV photon bombardment exhibited the most significant degradation, resulting in substantially reduced breakdown times and increased leakage currents. Thus both charged particle and photon bombardment degrade TDDB.

[i] E. T. Ogawa, J. Kim, G. S. Haase, H. C. Mogul, and J. W. McPherson, *Proc. IEEE Int. Rel. Physics Symp.*, p. 166. (2003)

[ii] Kok-Yong Yiang, H. W. Yao, A. Marathe, and O. Aubel, *Reliability Physics Symposium Proceedings, 44th Annual IEEE International* (2009).

[iii] F. Chen, O. Bravo, K. Chanda, P. McLaughlin, T. Sullivan, J. Gill, J. Lloyd, R. Kontra, J. Aitken, *Reliability Physics Symposium Proceedings, 44th Annual IEEE International* (2006)

[iv] C. Guedj, E. Martinez and G. Imbert, *Mater. Res. Soc. Symp. Proc.* **990** (2007)

4:40pm PS+EM-WeA9 Modeling the Penetration of Vacuum Ultraviolet Photons in Porous-ULK Films, *J. Lee, D.B. Graves*, University of California, Berkeley

VUV radiation inherent in plasma discharges have been shown to be a concern during plasma processing of low-*k* materials [1, 2]. VUV photons are known to break Si-C bonds, thereby transforming the material into a SiOx-like material post-exposure. Damage to samples exposed to a Xe VUV lamp ($\lambda = 147$ nm) in a vacuum chamber compared to corresponding effects in an Ar/O2 plasmas ($\lambda = 104$, 106, and 130 nm) suggests that chemical modification is limited by the penetration depth of the VUV photons, which is in turn dependent on wavelength. The formation of a SiOx-like layer near the surface of the material, which deepens as more carbon is lost, introduces a dynamic change of integrated VUV absorption throughout the material over time. As a result, the rate of carbon loss is continuously changing during the exposure. We present a model that captures this dynamic behavior and compare the model to experimental data by fitting a parameter that represents the effective carbon photolysis using a procedure described previously [3]. For sample exposures to argon plasmas, the model shows good agreement with the experimentally obtained carbon loss profile, inferred from post-processing, ex-situ Fourier transform infrared spectroscopy (FTIR). For O2 plasma, there is evidence that an additional effect, perhaps oxygen radicals, plays a major role in chemical modification at short times near the surface of the material. By contrast, we conclude that VUV photons contribute more to damage in the bulk. By exposing samples to VUV radiation in He plasmas ($\lambda = 58$ nm), it may be possible to treat and modify the surface of low-*k* films with high energy, low penetrating VUV photons to limit damage to the near-surface.

[1] B. Jinnai, T. Nozawa, and S. Samukawa, J. Vac. Sci. Tech. B **26**, 1926 (2008).

[2] J. Lee and D. B. Graves, J. Phys. D: Appl. Phys. **43**, 425201 (2010).

[3] M. J. Titus, D. G. Nest, and D. B. Graves, J. Phys. D: Appl. Phys. **42**, 152001 (2009).

5:00pm PS+EM-WeA10 Characterization of Plasma-Induced Damages on Low-k during Interconnection Integration by Scatterometric Porosimetry, *R. Hurand*, STMicroelectronics, France, *M. Darnon, T. Chevolleau, D. Fuard,* CNRS-LTM, France, *F. Bailly, R. Bouyssou,* STMicroelectronics, France, *T. David,* CEA Leti, France, *O. Joubert,* CNRS-LTM, France, *F. Leverd,* STMicroelectronics, France

With the continuous downscaling of devices, interconnects get narrower and narrower, and necessitate using porous low-k as insulator. Plasma processes required for the integration of low-k may cause damage at the sidewalls of the patterns, which degrades the dielectric properties of the material. The impact of the modified layer on the low-k sidewalls is becoming more critical when interconnects dimensions are scaled down. Developing low-damage plasma processes for porous low-k materials integration is compulsory, but requires a trustworthy characterization technique. Electron microscopy which leads to material shrinkage and does not precisely reveal the damaged layers is reaching its limitations. A new characterization technique, so-called Scatterometric Porosimetry has been recently proposed (Bouyssou et al. JVSTB, 2010). In this paper, we explain the principles of the method and demonstrate it can be used on complex industrial-relevant dielectric patterns (more than 9 dielectric layers, 140nm pitch). This technique can also be used to determine fundamental mechanisms of plasma induced modification to porous low-k dielectrics.

Scatterometric Porosimetry (SP) is a combination of scatterometry and porosimetric ellipsometry. Scatterometric measurements under vacuum give access to the pattern dimensions while measurements under controlled partial pressure of solvent give access to the material porosity or permeation (with low-polar solvent) or to the thickness of the hydrophilic damaged layer when water is used as a solvent.

Using this technique on an industrial stack, we determined the pattern profile and damaged layer thickness at the pattern sidewalls after each step of the etch process in a non destructive and high accuracy way. We identified that low-k main etch step is more damaging than barrier open or post etch plasma treatments: the damaged layer thickness representing 28% of the low-k width. On the contrary, the pattern profile is mostly controlled by the barrier opening step. A similar trend is measurable by SEM using decoration technique (measure before and after HF dip) but with less accuracy. We also investigated by SP the kinetic of sidewall modification during standard plasma processes including fluorocarbon-based processes or oxidizing or reducing plasma treatments.

5:20pm PS+EM-WeA11 Photon Effects in Damage of Porous Low-k SiOCH During Plasma Cleaning, *J. Shoeb*, Iowa State University, *M.J. Kushner*, University of Michigan

Porous dielectric materials offer lower capacitances that reduce RC time delays in integrated circuits. Typical *low-k* materials include SiOCH – silicon dioxide with carbon groups, principally CH_3, lining the pores. Fluorocarbon plasmas are often used to etch *low-k* materials, a process that leaves a fluorocarbon polymer on the *low-k* surface that must be removed. With porosities as high as 0.5, pores which are internally connected provide pathways for reactive species to enter into the porous network. During cleaning using oxygen plasmas, reactions of O atoms with the CH_x groups, can remove carbon as CO/CO_2. After the process, H_2O from air can form hydrophilic Si-OH which can further adsorb H_2O through hydrogen bonding or physisorption.[1] As such, O_2 plasmas can degrade the low *k* value of the porous SiCOH. Plasma cleaning with He/H_2 mixtures causes less damage to SiCOH as reaction of H atoms with –CH_3 is endothermic. These damage scenarios are complicated by the UV/VUV photons produced by the plasma. Photons produced by the plasma can break Si-C bonds and separate –CH_3 radicals from SiO_2 to enhance the C removal rate.[2] 130 nm photons of Ar/O_2 plasmas can penetrate into SiCOH ≈100 nm but photons of He/H_2 plasmas (<100 nm) penetrate ≈20 nm. As a result, VUV photons from O_2 plasmas can produce Si-C bond scission approximately 5 times deeper in the low-*k* material compared to the VUV photons from He/H_2 mixtures. These penetration depths are sensitive functions of porosity and interconnectivity. For example, penetration depth increases nearly linearly with increases in interconnectivity due to the alignment of pores. In this talk, we discuss results from modeling of the plasma damage of porous SiOCH in He/H_2 and Ar/O_2 plasmas. The HPEM (Hybrid Plasma Equipment Module) was employed to obtain the ion energy and angle distributions of reactive fluxes from inductively coupled plasmas. These are used as input to the MCFPM (Monte Carlo Feature Profile Module) with which profiles of the low-*k* materials after the plasma exposure are predicted. The role of photons in porous SiCOH damage and validation of numerical results will be discussed in terms of treatment time, interconnectivity and photon flux. Overall, we found that due to its lower photon penetration depth and less reactivity, He/H_2 plasmas cause approximately 3 times less damage than Ar/O_2 plasmas, which is in agreement with experiments.

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2. B. Jinnai, S. Fukuda, H. Ohtake, and S. Samukawa, J. Appl. Phys. **107**, 43302 (2010).

* Work supported by Semiconductor Research Corp.

5:40pm PS+EM-WeA12 X-ray Photoelectron Spectroscopy Investigation of the Schottky Barrier at BN/Cu Interfaces, *M. French, M. Jaehnig, M. Kuhn, J. Bielefeld, S. King, B. French*, Intel Corporation

Due to a low dielectric constant (4-4.5) and high density (1.8-2.0 g/cm³), Plasma Enhanced Chemically Vapor Deposited (PECVD) boron nitride (BN) is an intriguing material for use in low-k/Cu interconnect structures as a Cu diffusion barrier material. However, relatively little is known about the electrical leakage performance of BN in Cu interconnects or the Schottky barrier formed at the interface between these two materials. In this regard, x-ray photoelectron spectroscopy (XPS) was utilized to determine the Schottky barrier formed at the interface between polished Cu substrates and PECVD BN thin films. Our measurements indicate a barrier height of 3.0± 0.2 eV for the BN/Cu interface. This barrier height is nearly 2X that determined for a-SiCN:H and a-SiOC:H Cu capping layers and is attributed to the significantly larger band gap of BN (> 5 eV).

Plasma Science and Technology Division
Room: 201 - Session PS-WeA

Plasma Sources
Moderator: S.C. Shannon, North Carolina State University

2:00pm PS-WeA1 Integrated Power Delivery Systems for Next Generation Plasma Processes, *F.G. Tomasel, M. Watanabe, D. Carter*, Advanced Energy Industries

The continued drive for ever shrinking features in semiconductor manufacturing poses significant challenges for tool manufacturers and process developers. Requirements such as higher uniformity, tighter control of critical dimensions, reduced plasma damage, thinner layers, and shorter process times, combined with the introduction of new materials demand higher sophistication in the development of semiconductor processing tools, starting at the plasma chambers and going all the way

down to the power delivery systems. As an example, major advances in etch processes have been enabled by the introduction of a recent generation of RF power supplies with advanced capabilities, including frequency tuning while pulsing and multi-generator synchronized pulsing [1]. While significant improvement to a variety of plasma processes has been realized through the use of these high performance generators, a more holistic analysis of current power delivery systems seems to indicate that the characteristics and quality of the power delivered to the plasma load could be partly limited by power delivery system architectures based on autonomous building blocks. This observation suggests that a higher level of integration in communication, measurement and control among the components of the power delivery system could further benefit the development of next generation processes and tools. In this presentation we will show results from a new generation of power delivery systems where the matching networks and generators are fully integrated from a communication, measurement and control point of view. Although certainly possible, this integration scheme does not necessarily imply full physical integration. The performance of the integrated hardware combined with high performance control algorithms on both fixed and dynamic loads will be discussed in terms of electrical measurements performed at the loads under various operating regimes, including match and frequency tuning while pulsing. The results will demonstrate the potential for these integrated systems to enable processes with stringent requirements such as highly accurate power regulation in a wide dynamic range, faster power stabilization during transients, and minimal reflected power, both in pulsing and CW modes.

[1] C. Petit-Etienne, M. Darnon, L. Vallier, E. Pargon, G. Cunge, F. Boulard, O. Joubert, S. Banna, and T. Lill, J. Vac. Sci. Technol. B 28(5), 926 (2010).

2:20pm PS-WeA2 Remote VHF Source for High Efficiency Plasma Generation, *D. Carter*, *D.J. Hoffman, R. Grilley, K. Peterson*, Advanced Energy Industries
Remote plasma sources have evolved through the years and have generally been designed around traditional MF/HF frequencies in the 0.5 to 13 MHz range or at microwave frequencies around 2 GHz. Remote plasma sources can offer benefits including high dissociation rates, segregation of ionic and neutral species and reduced damage compared to in-situ generated plasmas. Due to the complexities of operating a microwave discharge or the difficulties achieving and maintaining H-mode ICP coupling, these devices are commonly designed for specific applications, such as chamber cleaning, organic layer ashing or PFC destruction in process effluent. As a result, many existing remote source technologies suffer from operating range and/or scaling constraints and so utilization in processes outside their specified purpose is often restricted.

This paper describes a new remote source technology employing a high efficiency VHF electrostatic coupling method to produce a versatile and robust remote plasma generator. The design approach is shown capable of producing high density discharges across a broad range while operating at relatively low voltages. The concept is scalable and adaptable to most any chemistry used for cleaning, etching and even deposition. This paper describes some of the important design elements incorporated into these new source devices along with early results illustrating a broad performance range exceeding many capabilities of the alternative technologies.

2:40pm PS-WeA3 Study of Radio Frequency Breakdown Mechanisms in a Plasma Environment, *J.B.O. Caughman*, *R.H. Goulding, D.A. Rasmussen*, Oak Ridge National Laboratory, *C.H. Castano Giraldo, M. Aghazarian*, University of Illinois at Urbana Champaign, *E.H. Martin, S.C. Shannon*, North Carolina State University **INVITED**
Radio frequency (RF) breakdown/arcing is a major power-limiting factor in antenna systems used for RF heating and current drive in magnetic fusion experiments and is also an issue for high voltage substrate operation in process plasmas. The factors that contribute to breakdown include gas pressure, gas type, magnetic field, materials, ultraviolet light, and local plasma density. The effects of these factors on RF breakdown are being studied in a resonant 1/4-wavelength section of vacuum transmission line terminated with an open circuit electrode structure with a well-defined electric field. A small plasma source is used to inject plasma into the high-field region of the electrodes. Changes in the electrical parameters, such as input impedance and the voltage at the electrodes, are being monitored to detect the breakdown events. Measurements of the light emission prior to and during an arc are also being made. For high vacuum conditions using copper electrodes, bright spots (unipolar arcs) appear on the electrode surfaces prior to a breakdown event. The voltage-current characteristic in this regime is consistent with Fowler-Nordheim field emission. An increase in the RF field results in an arc and a flash of light corresponding to copper line emission. Analysis of the electrode surfaces show large areas of

melting and formation of micron-sized rounded protrusions, especially along the sharp edges of small scratches or at impurity inclusions on the surface. The maximum electric field that can be sustained without breakdown is on the order of 30-40 kV/mm for vacuum conditions, but this value is substantially reduced in the presence of plasma and magnetic field. An increase in the chamber pressure results in a decrease in the maximum RF electric field that can be sustained without breakdown as the pressure approaches a few mTorr. The breakdown event leads to formation of a plasma in the structure, and the addition of an external magnetic field causes the formation of a plasma at lower pressures. Ultra-violet light, with an energy greater that the work function of the electrode material, has been shown to induce electron emission from the surface and initiate multipactor discharges. In addition, we are using optical emission spectroscopy to determine the magnitude of the DC and RF electric fields near the electrode structure by utilizing the dynamic Stark effect. Experimental details and future research directions will be presented.

4:00pm PS-WeA7 A Narrow Ion Energy Distribution Bias System, *V. Brouk*, Advanced Energy Industries, *S.C. Shannon*, North Carolina State University, *D.J. Hoffman, D. Carter, W. Hattel*, Advanced Energy Industries
Conventional bias systems use sine wave voltage systems to achieve ion energy distribution functions for the creation of thin films. By combining dual frequency sine waves, the mean energy and its spread can be independently controlled[1]. Arbitrary wave-shaping has been suggested to create single energy near-delta function distributions[2]. We investigate a system where the waveform is defined a priori where two elements are run in a feed forward system to control the instantaneous IEDF. We evaluate the effectiveness of this system in an argon/oxygen plasma at typical operating pressures inside the 10-150 mT range at plasma densities in the low 10^{10} cm^{-3} range.

1 S. Shannon et al.; J. Appl. Phys. 97, 103304 (2005)

2 Wendt A. et. al., "Method and apparatus for plasma processing with control of ion energy distribution at the substrates", US Patent 6201208, March 13, 2001

4:20pm PS-WeA8 Effect of Multi-frequency Bias on Ion Energy Distribution in Inductively Coupled Plasma, *A. Agarwal*, *A. Balakrishna, S. Rauf, K. Collins*, Applied Materials, Inc.
Inductively coupled plasma (ICP) sources, commonly used for semiconductor and conductor etching, embody the concept of functional separation between plasma production and ion energy control, wherein the inductive coupling through the coils is only responsible for the plasma generation while the bias determines the ion energies. Plasma etching of microelectronics structures at advanced technological nodes (< 3x nm), especially complicated structures such as multi-gate MOSFETs and 3D memory stacks, are placing great emphasis on control of ion energy distributions (IEDs) to finely discriminate etching thresholds.[1] Sinusoidal biases typically provide broad IEDs, making such control difficult to achieve. One promising alternative is non-sinusoidal bias waveforms, which have been demonstrated to provide such control.[2] However, there are issues associated with passing non-sinusoidal signals through the finite impedance of the match, transmission line, and the substrate.

Multi-frequency bias is compatible with current manufacturing hardware, and has been successfully used for controlling IEDs in capacitively coupled plasmas.[3] This approach may be utilized to enable IED control in ICP etchers as well. We investigate the impact of multiple bias frequencies in this paper. A high frequency applied in addition to a relatively low frequency bias causes the sheath potential to vary in a complicated manner due to the non-linear nature of the sheath. As a result, IED exhibits a complex dependence on relative bias voltages and frequencies.

In this work, the effect of applying bias at multiple frequencies will be discussed using results from a computational investigation. The 2-dimensional plasma equipment model, HPEM[4], has been modified to enable power deposition at multiple frequencies on the same electrode. Results will be discussed for Ar/Cl$_2$ plasma utilizing a 13.56 MHz bias in addition to a bias at a different frequency in an ICP chamber. The additional frequency is varied over a wide range and its consequences assessed on the ion and radical flux and IEDs incident on the wafer. We found that, in addition to modulating the IEDs, the flux composition is different depending on the frequency due to the secondary plasma generation by the alternate frequency.

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[2] A. Agarwal and M.J. Kushner, J. Vac. Sci. Technol A **27**, 37 (2009).

[3] S. Shannon, D. Hoffman, J.-G. Yang, A. Paterson, and J. Holland, J. Appl. Phys. **97**, 103304 (2005).

[4] M.J. Kushner, J. Phys. D: Appl. Phys. **42**, 194013 (2009).

4:40pm PS-WeA9 Electron Energy Distribution at Electrode in a Low Pressure Capacitively Coupled Plasma, *S. Rauf*, *L. Dorf, A. Agarwal, K. Collins*, Applied Materials, Inc.

Low pressure (sub-20 mTorr) capacitively coupled plasmas (CCP) are playing an increasingly important role in technological applications. As the mean free path becomes commensurate with the discharge dimensions, the fluid assumptions inherent in plasma and sheath models start to break down and ought to be reexamined. We focus on one aspect of the CCP operation in this paper, namely the electron energy distribution (EED) at electrodes and surfaces, and use kinetic particle-in-cell (PIC) models to understand the temporal behavior of the EED. Kinetic results are compared to fluid representation of the EED at electrodes to identify deficiencies in the fluid model at low pressures and propose solutions.

The sheath at the plasma-surface interface ensures that the electrons remain confined in the bulk plasma. However, during certain phases of the radio-frequency (RF) cycle in a CCP, the sheath collapses and the electrons exit at the surface. Energy distribution of these electrons contains useful information about the bulk plasma and the sheath. One can probe into the energy characteristics of these electrons using dc probes embedded in the electrode. Analysis of the resulting probe data can be used to determine the electron temperature, the electron density, and the EED in the bulk plasma. If a fluid model is used for this analysis, the electrons are assumed to be governed by the Boltzmann relation where their density and flux depend exponentially on the sheath voltage. Electrons are however highly non-equilibrium near the sheaths in CCPs and the Maxwellian distribution assumption (implicit in the Boltzmann relation) is questionable. Furthermore, most probe analysis models are dc-based. Low pressure situations demand further scrutiny as even the bulk plasma EED tends to become non-Maxwellian.

1 and 2-dimensional PIC model of CCPs are used for this investigation. These models consider plasma chemistry using the Monte Carlo technique. Simulations are done for Ar and N_2 plasmas under a variety of conditions (13.56 – 60 MHz RF frequency, RF voltage of 100 – 500 V, 5 – 100 mTorr gas pressure). The 1-dimensional PIC model is used to examine the EED at the electrodes where the sheath undergoes substantial variation during the RF cycle. The 2-dimensional model is used to investigate the EED at small metal surfaces (e.g., a probe) away from the primary electrodes. Dc voltage is also applied to the probe electrode in the 2-dimensional simulations. It is found that, in addition to a non-Maxwellian contribution from electrons adjacent to the sheath, the EED also contains high energy electrons which are the remnant of electrons that were accelerated at the opposite sheath.

5:00pm PS-WeA10 The Control of Electron Shading and Plasma EED*f* in a DC/RF Parallel-Plate Etcher, *L. Chen*, Tokyo Electron America
INVITED

There are several principles in the consideration of plasma etcher design. This paper addresses two important areas: (1) the ability of tailoring the electron energy distribution function (EED*f*), (2) the ability of adjusting the charging and neutralization of surface features (the electron shading effect). Stochastic heating by high frequency RF (VHF) energizes the Maxwellian bulk into the energetic tail population for efficient ionization. Such energetically bottom-up heating also indiscriminately populates the below-ionization energetic group that drives chemistry such as molecular dissociation and VUV production. A generic DC/RF system has a RF biased wafer-electrode with a high-negative DC superimposed opposing electrode. The DC/RF system dominates its electron heating with an energetically top-down process. The secondary electrons emitted from the high-negative DC surface disseminate the beam-energy into a distribution of energetic-electrons through collisions and more importantly, various beam-wave instabilities. These energetic electrons are trapped between the sheaths of the two parallel plates when the RF sheath field is sufficiently strong, dissipating their energies mainly into ionization. The energetic part of the EED*f* reveals (in descending order) a group of ballistic-electron associated with the applied –DC voltage, an energy continuum, and finally stop at a lower middle-energy peak in the range of ~ 40eV to 300eV depending on the process. The data show extremely efficient ionization by these energetic electrons and as a result, the Maxwellian bulk remains relatively unchanged at T_e~1.8eV regardless the bias RF power and process pressure. Such energetically decoupled EED*f* enables increased ionization without increasing molecular dissociation. In one RF period, the trapping of these energetic electrons diminishes as the RF sheath collapses. By pulse-synchronizing the –DC voltage and the bias RF voltage, ion-bombardment excitation of the wafer surface can alternate with high-energy electron-bombardment neutralization of the wafer surface. Ion-bombardment of the wafer surface occurs when the bias RF pulse is high and the –DC pulse is at a medium level. As the RF and the DC pulses are synchronously altered to a low RF voltage and a high-negative DC voltage, ion-bombardment excitation of the wafer diminishes and the wafer surface sees an increased current of energetic (>25eV) electrons. High aspect ratio SEM data show that the signatures of electron shading (*e.g.,* bending and twisting of the

features) are eliminated when synchronous DC/RF pulsing is implemented allowing energetic electrons to reach the bottom of high aspect ratio features.

5:40pm PS-WeA12 Negative Plasma Potentials Produced by Electropositive Plasmas in a Multi-Dipole Chamber, *N. Hershkowitz*, University of Wisconsin-Madison, *L. Oksuz,* Suleyman Demirel University, Turkey, *J.P. Sheehan*, University of Wisconsin-Madison

Negative plasma potentials were obtained in DC hot filament unmagnetized electropositive argon plasma in two configurations. For sufficiently low plasma density ($<10^6$ cm^{-3}) bounded by conducting walls, double layers provide ion and electron confinement near the walls. Similar results were observed in higher density plasmas ($\sim 10^9$ cm^{-3}) when a thin dielectric coating of oil covered the surface of the conducting walls. The potential profiles, measured using emissive probes in the limit of zero emission, from the center of the plasma to the potential minima are quite similar in shape to those observed when the plasma has positive plasma potentials. The primary electrons emitted from the filaments are important for charge conservation and for modification of the Bohm criteria but are not important for current balance.

Advanced Surface Engineering Division
Room: 104 - Session SE+PS-WeA

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

2:00pm SE+PS-WeA1 An Investigation of the Influence of Hybrid Current Modes on the Plasma Behavior during Plasma Electrolytic Oxidation (PEO) Coating Process on Mg and Mg- Alloys, *R.O. Hussein*, *D.O. Northwood, X. Nie*, University of Windsor, Canada

The increased use of magnesium alloys is considered one of the more promising methods for light-weighting in the automotive industry since, for a given strength level, Mg represents a 57% weight reduction over steel and 8% weight reduction over aluminum. However, due to its high chemical and electrochemical activity, magnesium has poor corrosion resistance in aqueous and other environments. In order for Mg and its alloys to find increased usage, there is a need to surface engineer these materials for improved corrosion and wear resistance. Plasma Electrolytic Oxidation (PEO) is an electrochemical process working at atmospheric pressure that uses an environmentally-friendly aqueous electrolyte to oxidize the metal surfaces to form ceramic oxide coatings which impart a high corrosion and wear resistance. The properties and structure of PEO coatings are dependent on parameters such as substrate metallurgy, composition of the electrolyte and the process conditions including current density, current mode and processing time. In this study we investigated the effect of current mode on plasma temperature and coating properties of PEO coatings formed on pure magnesium and an AM60B magnesium alloy (mass fraction: Al 5.6–6.4%, Mn 0.26–0.4%, Zn ≤ 0.2%, balance Mg). Unipolar, bipolar and hybrid (combination of both) current modes were used in this work. Optical Emission Spectroscopy (OES) was employed to study the plasma species, and electron temperature of the plasma. The morphology and microstructure of the coatings were investigated using Scanning Electron Microscopy (SEM). Potentiodynamic polarization in a 3.5% NaCl solution was used for the corrosion investigations.

2:20pm SE+PS-WeA2 Aging Mechanism of the Hydrophilic Silicon (100) Native Oxide Surface, *T.S. Williams*, *R.F. Hicks*, University of California Los Angeles

The wetting behavior of surfaces is important in many applications, such as for example, microfluidic devices that are fabricated on silicon wafers. In this study, silicon native oxide surfaces were cleaned with a radio frequency, atmospheric pressure helium and oxygen plasma and with ammonium hydroxide, hydrogen peroxide, and deionized water in a 1:1:5 ratio (RCA SC-1). Both processes created a hydrophilic state with water contact angles of <5° and 16.2±1.7°, respectively. During subsequent storage in a chamber purged with boil off from a liquid nitrogen tank, the water contact angle increased over several days at a rate dependant on the cleaning method used. Internal reflection infrared spectroscopy revealed that the change in water contact angle was due to the adsorption of organic molecules with an average hydrocarbon chain length of 10±2. The rate of the adsorption process decreased with the fraction of hydrogen-bonded

hydroxyl groups on the surface relative to those groups that were isolated. On Si (100) surfaces that were cleaned by RCA SC-1 and the plasma, 96% of the silanol groups were hydrogen bonded. The first-order rate constant for adsorption of the organic contaminant on this surface was 0.182 ± 0.008 hr^{-1}. Several methods have been explored for keeping the silicon dioxide surface in a hydrophilic state for extended periods of time, and these will be presented at the meeting.

2:40pm SE+PS-WeA3 Polyimide Surface Treatment to Hydrophobic Surface with Self Assembled Mask Layer for Direct Inkjet Patterning Process, *J.B. Park*, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

The inkjet printing technology is emerging as one of the important process technologies for electronics, because it can significantly reduce the manufacturing process cost, materials waste, and number of process steps. Especially, many researchers investigating the inkjet-printed process have focused their attention on the printing of conductive films on a polymer film. The technique is not suitable for applying to organic transistors yet, because its pattern width is limited to several dozens μm by statistical variations of the flight direction of droplets and their spreading on the substrate.

In this study, polyimide film was treated to hydrophobic surface using modified atmospheric pressure plasma system (double discharge system). Especially, for keeping the surface characteristics permanently, surface of the polymer film was etch/textured with self assembled mask layer to form the textured polymer surface. The texturing process is progressed for 4 process step. The mask layer(HMDS) is deposited and agglomeration/oxidation by using atmospheric discharge of $HMDS/He/O_2$ gas mixture through 1st step and 2nd step . And Etch and texturing process is progressed with atmospheric discharge of $He/O_2/Ar$ gas mixture in 3rd step. And the mask layer is removed in 4rd step using NF_3/N_2 gas mixture of remote atmospheric plasma. In the 2nd process, the HMDSO mask layer is formed specific tissue layer as the input power was increased. And the morphology is also varied with the whole size of the HMDSO mask layer. And this whole process is possible because of perfect etch selectivity between the polyimide film and HMDSO layer. The contact angle of textured polyimide film was measured over the 100 degree and varied with textured surface morphology. And keeping the pattern width of inkjet printing was clearly improved compare with normal polymer surface.

3:00pm SE+PS-WeA4 In Situ Fabricating Blue Ceramic Coatings on Al Alloy by Plasma Electrolytic Oxidation, *Z.J. Wang*, *R.O. Hussein*, *X. Nie*, *H. Hu*, University of Windsor, Canada

In-situ formation of novel blue ceramic coatings on Al alloy with a controllable blue color was successfully achieved using a plasma electrolytic oxidation (PEO) process working at atmospheric pressure. This novel blue ceramic coating overcomes the shortcomings of surface treatments resulting from traditional dyeing process by depositing organic dyes into the porous structure of anodic film, such as poor resistance of abrasion and rapid fading when exposed to light. X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy were employed to characterize the microstructure of the blue ceramic coating. The main compositions of the coating are $CoAl_2O_4$ and Al_2O_3. This work shows that the working current density plays significant roles on $CoAl_2O_4$ phase in the ceramic coating which has a controllable influence on the coating color. Low current density reduces the percentage of $CoAl_2O_4$ component in the coating, and light blue ceramic is produced. On the other hand, higher current density increases $CoAl_2O_4$ component in the coating, hence deep blue ceramic is fabricated. Electrochemical test, ball-on-plate sliding wear tester and thermal shock method were utilized for the corrosion, wear and thermal shock resistance analysis of the fabricated ceramic coatings. The results indicate that the developed blue coating via PEO process superiorly improves the tribological property, anti-corrosion property and thermal shock resistance. The fabricated blue ceramic coating tends to be applied to colored light cast alloys for applications used in relatively harsh and severe working environments.

4:00pm SE+PS-WeA7 Cold Atmospheric Plasma Sources for Treatment of Cell-Containing Surfaces, *M.G. Kong*, Loughborough University, UK **INVITED**

Low-temperature gas discharges generated at atmospheric pressure, commonly known as cold atmospheric plasmas, are a relatively new member of the processing plasma family. Without the need for a vacuum chamber, they offer a much more cost-effective route to material processing and open up opportunities for chamber-less processes and vacuum-incompatible materials such as moist objects. With a mean electron energy at a few eV and a gas temperature close to room temperature, cold atmospheric plasmas are ideally placed for effective chemical dissociation and hence for a wide range of materials processing applications. In this

contribution, a review of the current cold atmospheric plasma sources will be presented in terms of their underpinning science and their current technology capability. These include the traditional dielectric barrier discharges, radio-frequency glow discharges, and cold atmospheric plasma jets and jet arrays. Through discussion of their plasma characteristics, their applications are exemplified through treatment of cell-containing surfaces, including living tissues. The interaction of cold atmospheric plasmas with individual microorganisms and indeed microbial communities will be discussed, and its implications to treatment of skin diseases and wounds will be presented. This will also be supported with data of plasma interaction with mammalian cells.

4:40pm SE+PS-WeA9 High Performance of 60-Hz Atmospheric Pressure Plasma: Basic Characteristics and Applications, *F. Jia*, *K. Takeda*, *K. Ishikawa*, *H. Inui*, *S. Iseki*, Nagoya University, Japan, *H. Kano*, NU Eco-Engineering Co., Ltd., Japan, *H. Kondo*, *M. Sekine*, *M. Hori*, Nagoya University, Japan

In this paper, the spatial distribution of atomic oxygen density in a 60-Hz non-equilibrium atmospheric pressure plasma[1] is diagnosed by two-photon absorption laser induced fluorescence (TALIF)[2] . The plasma unit is made of ceramics comprised three regions: gas diffusion region, main discharge region, and plasma jet in the open air. The discharge gases were Ar and a small amount of O2. The plasma could offer electron density as high as 1015 cm-3 with a low gas temperature[1,3], and have been successfully used to clean glass surface[1]and inactivate the spores of Penicillium digitatum[4]. In the above applications, we find that atomic oxygen plays an important role[1,4], and the samples are usually treated in the open air; therefore it is necessary to investigate the behavior of atomic oxygen, especially in the open air, in order to achieve high performance. A dye laser pumped by an excimer laser is used to generate nanosecond UV laser pulses at around λ= 226 nm for the two-photon excitation of atomic oxygen ($2p$ $3P$−$3p$ $3P$). The laser power is adjusted to 0.1 mJ/pulse to make sure that the effect of photo dissociation of ozone can be negligible in the experiment. The results showed that the effect of O2 admixture variation on the atomic oxygen density is totally different in the main discharge region and in the plasma jet. In the main discharge region where the discharge gas are only Ar and O2, the density of atomic oxygen increased quickly with adding only 0.25% O2, became saturated with adding 1% O2, and reduced quickly when adding 1.5% O2. The discharge was stable until adding 2.5% O2. However, in the plasma jet that was in the open air, the density of atomic oxygen remained almost same while adding O2 from 0% to 2.5%. This is because the mechanisms of generation and recombination of atomic oxygen are different in the main discharge region and plasma jet. More work will be done to study the behavior of atomic oxygen in the plasma jet, the data and results will be very useful to understand the behavior of atomic oxygen and improve the applications of non-equilibrium atmospheric pressure plasma. [1] M. Iwasaki, H. Inui, Y. Matsudaira, H. Kano, N. Yoshida, M. Ito, and M. Hori, Appl. Phys. Lett. **92**, 081503 (2008). [2] K. Niemi, V. Schulz-von der Gathen, and H. F. Dobele, Plasma Sources Sci. Technol. **14**, 375 (2005). [3] Fengdong Jia, Naoya Sumi, Kenji Ishikawa, Hiroyuki Kano, Hirotoshi Inui, Jagath Kularatne, Keigo Takeda, Hiroki Kondo, Makoto Sekine, Akihiro Kono, and Masaru Hori, Appl. Phys. Express, **4**, 026101 (2011). [4] S. Iseki, T. Ohta, A. Aomatsu, M. Ito, H. Kano, Y. Higashijima, and M. Hori, Appl. Phys. Lett. **96**, 153704 (2010).

5:00pm SE+PS-WeA10 Dense Atmospheric Pressure Discharges for Surface and Gas Treatment, *M.J. Kelly*, *B.D. Schultz*, *W.M. Hooke*, International Technology Center

Dielectric barrier discharge (DBD) plasmas have been formed in atmospheric pressure gases exhibiting peak currents in excess of 100 amperes. Power densities during the pulse routinely exceed 100 kilowatts per cubic centimeter for moderately sized electrodes (>100 square centimeters) with ionization densities of 10^{14} per cubic centimeter. Charge transfer of 100 microcoulombs per pulse has been repeatedly generated at frequencies up to 100 hertz, and the charge delivery is found to scale in proportion to the electrode area for a given dielectric consistent with a homogeneous discharge. Diffuse discharges have been formed over larger areas (exceeding 1 meter in length and 500 square centimeters) as well. These results were obtained using a custom high voltage driving source and in the absence of helium, argon, or any other easily ionized gas. The source readily achieves an overvoltage in excess of the DC breakdown voltage prior to the onset of breakdown in which 20-30 kV is delivered with rise times shorter than the lag time between the pulse crossing the threshold voltage and the onset of a discharge. Electrical modeling of the discharge characteristics has produced correlations relating power and charge transfer to various electrical and geometrical parameters of the system which will be discussed in this paper.

5:20pm SE+PS-WeA11 Investigation of Discharge Modes of Cylindrical Dielectric Barrier Discharge Configuration for Surface Treatment at Atmospheric-Pressure, *T.S. Cho, Y.L. Wu, J.M. Hong, Z. Ouyang, D.N. Ruzic*, University of Illinois at Urbana Champaign

To date, various structural concepts of atmospheric-pressure dielectric barrier discharge had been studied and some of the concepts have already been commercialized for surface treatment processes because of its simplicity and scalability. In this study, cylindrical dielectric barrier discharge configurations for treating the powder particles or controlling the air pollutants at atmospheric-pressure have been investigated. The electrical characteristics of the cylindrical dielectric barrier discharge structure as a capacitive load have been experimentally measured for the mixture of helium and nitrogen and its flow rate with voltage-charge lissajous analysis method. Also, it has been compared with remote plasmas from the commercial planar dielectric barrier discharge system of which capacitance has been 280pF for driving conditions of 5kV and 30 kHz. Emissions from the atmospheric-pressure dielectric barrier discharge plasma have been analyzed for varied gas conditions with the optical emission spectroscopy. For comparison purposes, the glass substrates treated with commercial planar and cylindrical dielectric barrier discharge plasmas have been analyzed. In addition, the sugar-alcohol particles have been treated with atmospheric-pressure plasma from the cylindrical dielectric barrier discharge system, and compared with the untreated particles.

Thursday Morning, November 3, 2011

Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM

Spectroscopic Ellipsometry of Biological Materials and Organic Films
Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates, *K.-J. Eichhorn*, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**
Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature Tg of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having different architectures and functional groups /2/. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The Tg data were determined from the ellipsometric results and discussed.

In the second part, "smart" surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a "grafting-to" procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNIPAAM) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry /3,4/.

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/2/ M. Erber, A. Khalyavina, K.-J. Eichhorn, B. Voit, Polymer51 (2010), 129-135

/3/ E. Bittrich, M. Kuntzsch, K.-J. Eichhorn, P. Uhlmann, J. Polym. Sci. B, Polym. Phys.48 (2010), 1606-1615

/4/ Y. Mikhailova, L. Ionov, J. Rappich, M. Gensch, N. Esser, S. Minko, K.-J. Eichhorn, M. Stamm, K. Hinrichs, Anal. Chem.79 (2007)20, 7676-7682

8:40am EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles, *S. Rauch*, Leibniz-Institut für Polymerforschung Dresden e. V., Germany
Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(*N*-isopropylacrylamide) (PNiPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g. Fe_3O_4 or $CoFe_2O_4$) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how much nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of Fe_3O_4-NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNiPAAm with hydrophobic Fe_3O_4-NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of Fe_3O_4 with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized Fe_3O_4-NP onto PNiPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

9:00am EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties, *C. Akerlind*, Swedish Defence Research Agency / Linköping University, Sweden, *H. Arwin,* Linköping University, Sweden, *T. Hallberg, H. Kariis,* Swedish Defence Research Agency, Sweden, *J. Landin, K. Järrendahl,* Linköping University, Sweden
Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25 μm were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39 μm, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant BRDF for most angles, *i.e.* the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization *P* even for nonpolarized incident light. The angular dependence of *P* was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison, *P* was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

9:20am EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation Characterization of Biomolecule Adsorption within Sculptured Thin Films, *T. Kasputis, D. Schmidt,* **K.B. Rodenhausen**, *H. Wang, A.K. Pannier, M. Schubert*, University of Nebraska - Lincoln
Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller

proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

9:40am EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation*, J.Y. Gerasimov**, K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert*, University of Nebraska - Lincoln*
DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry*, L.J. Richter, C. Tarrio, S. Grantham, S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology*, N.S. Faradzhev,* University of Virginia*
Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing of the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical ("witness plate") studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1 mm. Both ex-situ, small spot mapping spectroscopic ellipsometry (SE) and in situ single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry*, J.P. Piel, **L. Kitzinger**, A. Bondaz, C. Defranoux,* SEMILAB-SOPRALAB, France*
Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+NS+PS+SS-ThM

Graphene: Surface Chemistry, Functionalization, Plasma Processing and Sensor Applications
Moderator: G.G. Jernigan, U.S. Naval Research Laboratory

8:00am GR+NS+PS+SS-ThM1 Tailoring Graphene's Properties through Chemistry*, J.T. Robinson*, Naval Research Laboratory **INVITED**
Graphene's unique electron transport properties have motivated intensive research and development to mold it into the electronic material of the future. However, graphene can be much more than an electrical switch. Its high structural integrity and chemical flexibility enable extensive control of its optical, mechanical, and electronic properties. The most scalable and inexpensive route to modify these properties is chemical functionalization. Consequently, chemically modified graphenes (CMGs) have emerged as a system of materials whose many attractive properties complement and extend those of unmodified graphene.

In this talk I will describe efforts at NRL to synthesize and characterize new CMGs as well as first steps towards applications such as sensors and nanomechanical resonators. To begin, I will discuss the interaction of small molecules (CCl_4, CS_2, H_2O and acetone) with single-layer graphene under steady-state conditions using infrared multiple-internal-reflection. Adsorption-induced changes in the IR spectra suggest the formation of in-plane strain, where we observe important differences arising between species that form liquid-like layers under steady-state conditions and those that do not. Second, I will discuss graphene oxide, a well known derivative of graphene that has a rich ensemble of oxygen-based functional groups and related defects. These defects are readily tunable through chemical or thermal treatments and facilitate the formation of vapor and bio-sensors with parts-per-billion and nanomolar sensitivities, respectively. Third, I will discuss the stoichiometric addition of fluorine atoms to graphene and describe their resulting properties. Experiments indicate fluorinated graphene derivatives become highly resistive and optically transparent, while DFT calculations show band gaps open depending on the fluorine coverage and ordering. Finally, through combining these two material systems, I will discuss the fabrication and performance of CMG-based nanomechanical resonators. Through chemical modification, the frequency of CMG-based resonators is tunable over 500% and their quality factors can exceed 20,000 at room temperature.

8:40am GR+NS+PS+SS-ThM3 Water Splits Epitaxial Graphene on Ru(0001) from Domain Boundaries*, X. Feng, S. Maier, M. Salmeron,* Lawrence Berkeley National Laboratory*
Epitaxial growth of graphene on metal substrates has recently been demonstrated as a rational synthesis route for producing macroscopic graphene domains and may hold the key to realizing the potential of large-scale applications. However, the epitaxial graphene is generally polycrystalline, with domain boundaries that may severely affect its structure and properties. Here we report that water adsorption splits

epitaxial graphene on Ru(0001) and results in nanoscale graphene flakes at temperatures as low as 90K. Scanning tunneling microscopy studies indicated that the splitting starts primarily from domain boundaries followed by water intercalation underneath graphene. The mechanism proposed is that Ru-induced water dissociation provides hydroxyl species that break the graphene starting at the dangling and stretched bonds at the boundaries.

9:00am GR+NS+PS+SS-ThM4 Novel Strategies for the Chemical Functionalization of Graphene: Towards Graphene/Molecular Nanosheet Heretostructures, *A. Turchanin*, C.T. Nottbohm, Z. Zheng, M. Schnietz, A. Beyer, University of Bielefeld, Germany, *M. Heilemann, M. Sauer*, Julius-Maximilians-University Würzburg, Germany, *A. Gölzhäuser*, University of Bielefeld, Germany

Chemical functionalization of graphene is essential for implementations of the 2D carbon sheets in various functional devices (e.g. chemical and biochemical sensors, nanoelectromechanical components, etc.) and for tuning their electrical properties. However, the functionalization is difficult to achieve due to the chemical inertness of graphene sheets with high structural quality. On the other hand, ultrathin (~1 nm) molecular nanosheets made from self-assembled monolayers (SAMs) possess well-defined chemical groups intrinsically. Moreover, due to the directionality of the constituting molecules both faces of the free-standing nanosheets -*Janus nanomembranes*- can be independently and specifically functionalized. Simple mechanical stacking of the nanosheets allows fabricating ultrathin layered structures with tunable physical and chemical properties. Upon annealing these stacks are converted into graphene sheets with adjusted thickness. The engineering of graphene/nanosheet heterostructures opens up novel routes towards chemically functionalized graphene sheets for functional applications. A potential of this approach will be discussed.

Z. Zheng, C.T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Gölzhäuser, "Janus nanomembranes: A generic platform for chemistry in two dimensions", *Angew. Chem. Int. Ed.* 49 (2010) 8493-8497

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A. Turchanin, D. Weber, M. Büenfeld, C. Kisielowski, M. Fistul, K. Efetov, R. Stosch, T. Weimann, J. Mayer, A. Gölzhäuser, "Conversion of self-assembled monolayers into nanocrystalline graphene: structure and electric transport", *ACS Nano* 5 (2011) DOI: 10.1021/nn200297n

9:20am GR+NS+PS+SS-ThM5 Biosensors Based on Chemically Modified Graphene, *R. Stine*, J.T. Robinson, P.E. Sheehan, C.R. Tamanaha, U.S. Naval Research Laboratory

The sensitive and specific detection of biomolecules without using a label is a long-standing goal of the biosensors community. Several promising advances of the past several years formed biological field effect transistors (bioFETs) that have as the gate nanoscale materials such as nanowires and carbon nanotubes. The nanoscale dimensions of these materials allow the small charges associated with biomolecules to significantly change conduction through the gate. These conduction changes can be correlated with solution concentration to give precise readouts. While bioFETs are a promising way forward, there are many processing difficulties associated with these 1-D materials that inhibit large scale, reproducible fabrication of devices. Here, we will discuss our efforts to develop biosensors based on 2-D chemically modified graphene. These devices impart the sensitivity gains seen from other nanoscale materials, but offer a configuration that is amenable to processing techniques that are common in the semiconductor industry. We will focus primarily on chemically modifying graphene for attachment of biomolecular probes. Devices utilizing both graphene and graphene oxide will be covered, and surface spectroscopic studies of the material modification will be discussed. Successful results for the detection of specific DNA hybridization will also be presented, with detection limits that compare favorably with the best results reported from nanowire bioFETs.

Acknowledgements: R.S. is an employee of Nova Research Inc., Alexandria, VA, USA. This project received support from the Defense Threat Reduction Agency-Joint Science and Technology Office for Chemical and Biological Defense.

9:40am GR+NS+PS+SS-ThM6 Controllable Defect Healing and N-doping of Graphene by CO and NO Molecules, *B. Wang*, Vanderbilt University, *S.T. Pantelides*, Vanderbilt University and ORNL

Point defects alter strongly the physical and chemical properties of graphene, e.g. they degrade electrical transport and enhance chemical reactivity. Defects could also be used to achieve graphene functionalization,

e.g. N atoms, as n-type dopant, can be introduced to obtain n-type graphene. Thus, controllable defect healing and N-doping in graphene would be very valuable for potential device applications. Here we report first-principles molecular dynamic simulations that suggest a procedure for defect healing and N-doping with fast dynamics and low thermal budget. Vacancies in graphene can be healed by sequential exposure to CO and NO molecules. A CO molecule gets adsorbed at a vacancy site and a NO molecule subsequently removes the extra O by forming NO_2, which desorbs quickly resulting in a defect-free graphene sheet. Controllable N-doping can be achieved by sequential vacancy creation (e.g. by electron or ion beam) and subsequent exposure to NO molecules at room temperature. NO molecules are trapped at vacancies and other NO molecules remove the extra O atoms simultaneously, leaving N atoms incorporated in graphene. Both reactions (healing and doping) are exothermic. We suggest that a combination of CO and NO molecules can potentially provide simultaneous healing and doping. Adjusting the ratio could fine-tune the N-doping level. The proposed strategy introduces no extra defects and is promising for graphene-based electronic materials in radiation environments. Finally, we propose that NH_3, which is normally used in experiments to introduce N atoms, may not be a good choice for N-doping since the dissociated H atoms can be trapped at vacancies and act as impurities that increase the resistivity of graphene.

10:40am GR+NS+PS+SS-ThM9 Aptamer Modified Graphene Bio Sensor, *K. Maehashi*, Y. Ohno, K. Matsumoto, Osaka University, Japan

Since graphene has high mobility and a large surface area, it is suitable for the application of the high sensitive sensor. In the present paper, we have first succeeded in the selective detection of the bio molecule such as IgE using the aptamer modified graphene FET.

The graphene was formed using the conventional mechanical exfoliation method on the SiO 2 /Si substrate. The source and drain electrode were formed by the electron beam lithography and Ti/Au evaporation. The silicon rubber pool was formed on the fabricated graphene FET, and phosphoric buffer solution was poured into the silicon rubber pool. The Ag/AgCl reference electrode was introduced into the phosphoric buffer solution, which works as a top gate electrode for the graphene FET.

As a first step of the biosensor, three bio molecule such as Immunoglobulin E(IgE), Streptavidin(SA), and Bovine serum albumin(BSA) were introduced into the phosphoric buffer solution of pH of 6.8, and the change of the drain current of the graphene FET was detected. In this case, the IgE and SA shows the decrease of the drain current, while the BSA the increase of the drain current. Because, in the phosphoric buffer solution of pH of 6.8, IgE and SA are positively charged, while BSA negatively charged. Therefore, the hole current of the graphene FET change the drain current following the charge of the bio molecule. As a result, bare graphene FET can detect the bio molecule following the charge of the molecule, but it dose not have the selectivity

As a second step, in order to get the selective sensing of the bio molecule, the surface of the graphene was modified by the IgE aptamer, which was connected to graphene using the linker(1-pyrenebutanoic acid succinimidyl ester). IgE aptamer was known to selectively couple to IgE. When the BSA and SA were introduced into the phosphoric buffer solution on the aptamer modified graphene FET, there occurred no change in the drain current, while the IgE was introduced in the solution, the drastic decrease of the drain current was observed. This means the BSA and SA do not couple to IgE aptamer, and only IgE couple to the IgE aptamer on the grapehne FET. Therefore, the selective sensing of the IgE was successfully carried out.

We have first succeeded in the selective sensing of IgE using the modified graphene FET.

11:00am GR+NS+PS+SS-ThM10 A Molecular Dynamics Study of Chemical Modification of Graphene Oxide Sheets, *T. Liang*, B. Devine, S.R. Phillpot, S.B. Sinnott, University of Florida

Graphene, the single-layered graphite, has attracted tremendous attention owing to its fascinating physical properties. One of the main obstacles in this field is to find an efficient and consistent approach to produce graphene sheets in large quantities. In addition to the mechanical exfoliation method, many chemical approaches have been developed to synthesize graphene on a large scale. The key intermediate product in these chemical approaches is the graphene oxide sheets, which are often heavily oxygenated with hydroxyl or epoxide functional groups on the surface and carbonyl or carboxyl groups at the edge. However the energetic and kinetics associated with graphene oxide sheets have not been elucidated in detail due to the inherent chemical complexity of the system. Here, a new dynamic charge empirical potential is presented that is used in classical molecular dynamics

simulations to elucidate the dynamics of graphene oxidation and the resulting influence on their mechanical and structural properties. In addition, the oxygenating and hydrogenating processes of defective graphene sheets at room temperature in addition to elevated temperatures are presented. The findings are compared to the results of first principles density functional theory findings and to experimental data.

11:20am **GR+NS+PS+SS-ThM11** **Enhancing and Controlling the Chemical Reactivity of Epitaxial Graphene via Growth Induced Strain**, *J.E. Johns*, Northwestern University, *Md.Z. Hossain,* Gunma University, Japan, *M.C. Hersam*, Northwestern University

The high electrical and thermal conductivity of graphene, as well as its two dimensional nature, has led to its rapid incorporation into any practical applications including high frequency analog transistors and transparent conductors. However, many other potential applications, such as excitonic switches, psuedospin devices, or digital logic circuits, require covalent chemical modification of graphene. Due to the chemical inertness of its pi bonded network, previous methods for covalently modifying graphene have required extreme, irreversible conditions including acidic treatments, high energy radical polymerization, and ion beam implantation. Here we present an alternative method for increasing the chemical reactivity of graphene by systematically altering the compressive strain of epitaxial graphene (EG) on SiC(0001). Depending on its annealing history, EG has been shown to have a compressive strain of 0% to 1% due to a mismatch of thermal expansion coefficients with the underlying buffer layer and silicon carbide substrate. Using differing thermal treatments, we show that the amount of strain in EG can be tailored, as verified by characteristic peak shifts of the 2D Raman band. The resulting chemical reactivity of the strained EG is studied at the atomic-scale using ultra-high vacuum scanning tunneling microscopy following reversible gas phase reactions of EG with oxygen and fluorine. These results suggest a new method for controlling the electronic properties of graphene, and provide fundamental insight into the nature of chemical bonding on EG.

11:40am **GR+NS+PS+SS-ThM12** **Plasma-based Functionalization of Graphene with Primary Amines for Biomaterials Applications**, *S.G. Walton*, M. Baraket, S.C. Hernandez, R. Stine, W.K. Lee, C.R. Tamanaha, P.E. Sheehan, J.T. Robinson, C.E. Junkermeier, T.L. Reinecke, Naval Research Laboratory (NRL)

Graphene, a sp^2-structured monolayer of carbon atoms, has attracted much interest for its fundamental science and its potential in many device applications. By tailoring its surface chemistry, material properties can be regulated and thus broaden the number of potential applications. In this work, we demonstrate that by chemically functionalizing graphene the electrical properties and its interaction with adsorbates may be controlled. Electron beam generated plasmas produced in ammonia-containing gas, is used to controllably introduce nitrogen and primary amines. A study of the chemical, electrical and structural properties of the chemically-modified graphene at different functional group concentrations is discussed. In addition, the use of amine-functionalized graphene as a bio-sensing platform for DNA detection using a field-effect-transistor-based sensor is demonstrated. This work is supported by the Office of the Naval Research.

Plasma Science and Technology Division
Room: 202 - Session PS+TF-ThM

Plasma Deposition and Plasma Enhanced ALD
Moderator: S.-P. Tay, Mattson Technology Inc.

8:00am **PS+TF-ThM1** **High Quality SiNx by Microwave RLSA Plasma Enhanced Atomic Layer Deposition**, *T. Karakawa*, M. Oka, N. Fukiage, H. Ueda, T. Nozawa, Tokyo Electron Technology Development Institute, INC., Japan

Shrinking critical dimensions of Ultra Large Scale Integration (ULSI) and optical device structures continue to drive advances in semiconductor fabrication processes. Three dimensional (3D) and metal gate structures for example, require low temperature dielectric layers (e.g., SiO2 and SiNx) with dimensions and film quality that may be met only by Plasma Enhanced Atomic Layer Deposition (PEALD) [1]. In addition to film quality and conformality, minimizing plasma damage in the PEALD process sequence is imperative. Prior to this work we characterized PEALD SiO2 deposition in a Radial Line Slot Antenna (RLSA) plasma source using bis-tertiaryl-buthyl-amino-silane (BTBAS) as a precursor [2]. In this study, we determined RLSA ALD process conditions favorable for SiNx film formation. The Si ALD precursor was dichlorosilane (DCS) and nitridation employed a NH3, N2 and Ar RLSA plasma. The wafer temperature was controlled below 400°C during the ALD process. Precursor adsorption time,

process temperature, nitration time, plasma power were varied in order to determine the RLSA Plasma conditions resulting in the best SiNx ALD film quality. We obtained very high quality SiNx films having almost the same HF wet-etching rate as thermal LP-CVD SiNx (720°C) film. In this presentation, the results of Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) analyzed RLSA ALD deposited SiNx films will be presented. We found that the sub-nitride bonding ratio of the SiNx film was strongly correlated with the HF wet-etching rate, a measure of the film quality. The lower sub-nitride bonded SiNx film such as Si3N4 was created by the RLSA plasma at low temperature with low plasma damage. The reason so little damage occurs is the low rate of ion bombardment on new Si3N4 surfaces during plasma nitridation.

[1] S. Yokoyama et al., Applied Surface Science 112 (1997) 75-81

[2] Y. Osawa et al., Proceedings DPS-2009, 2-P51

8:20am **PS+TF-ThM2** **Composition, Morphology and Optical Dispersion of Plasma Polymerized Titanium Oxide Derived Using PECVD**, *L. Sun*, General Dynamics Information Technology, *A. Reed,* Air Force Resarch Laboratory, *H. Jiang,* General Dynamics Information Technology, *J.T. Grant,* University of Dayton Research Institute, *R. Jakubiak*, Air Force Resarch Laboratory

In this work plasma-polymerized (PP-) TiO_xC_y films derived from titanium (IV) isopropoxide (TTIP) were deposited onto Si and KBr substrates using remote, room temperature plasma enhanced chemical vapor deposition (PECVD). The composition and morphology of the films was varied by systematically changing the ratio of Ar to O_2 in the carrier gas. Chemical compositions were investigated by FTIR and X-ray photoelectron spectroscopy (XPS). Morphological data derived atomic force microscopy (AFM) and scanning electronic microscopy (SEM) studies showed that the morphology was strongly dependent on the ratio of oxygen to total carrier gas composition. The films grown with Ar as the majority carrier gas have a featureless, smooth, one phase 3-D crosslinking morphology due to the incomplete oxidation of Ti to the most stable Ti^{4+} valence state during deposition in an oxygen poor environment. As the mixture of carrier gas became more O_2 rich a second phase evolved that had a columnar structure attributed to TiO_2. This increase in oxidation was also noted in high resolution XPS measurements where a peak corresponding to a carboxyl group in the C 1s spectrum increases with increasing O_2 concentration. Development of the structured second phase was also noted in the optical dispersion obtained by spectroscopic ellipsometry. In order to fit the data, an anisotropic model has to be used that took into account the surface roughness determined from the AFM and SEM studies.

8:40am **PS+TF-ThM3** **Plasma Deposition of Carbide-Based Composite Membranes for Hydrogen Purification**, *C.A. Wolden*, Colorado School of Mines **INVITED**

We introduce a new class of composite membranes based on transition metal carbide as economical alternatives to palladium for high temperature purification of H_2. In this talk we describe two membrane concepts that were synthesized using plasma-enhanced chemical vapor deposition (PECVD) and magnetron sputtering. The first is a surface diffusion membrane comprised of nanostructured Mo_2C deposited on porous ceramic supports. Stoichiometric Mo_2C was fabricated using a two step synthesis process. Dense molybdenum oxide films were first deposited by plasma-enhanced chemical vapor deposition (PECVD) using mixtures of MoF_6, H_2, and O_2. Oxide films 100 – 500 nm in thickness were then converted into molybdenum carbide using temperature programmed reaction using mixtures of H_2 and CH_4. Permeation testing of these membranes showed very high flux, but limited selectivity. To address this issue we describe a counterflow PECVD approach that we are developing which is used to both modify the pore size of the original supports as well as to repair pinholes that develop during the carburization.

The second strategy is to produce dense composite membranes comprised of Mo_2C layers sputtered onto BCC metal foils. BCC metals (V, Ta, Nb) and their alloys have extremely high permeability for atomic hydrogen, but negligible catalytic activity for hydrogen dissociation. Platinum group metals have been used as catalysts, particularly palladium, but at elevated temperature they alloy with the underlying metal and rapidly lose their activity. In contrast, the Mo_2C/V membranes described in this work displayed no change in permeability when operated at high temperature for >160 hours, and transmission electron microscopy confirmed that negligible interdiffusion occurs between these materials during testing. Hydrogen dissociation is the primary factor limiting hydrogen transport, as evidenced by the sensitivity of performance to carbide morphology. Sputter parameters were systematically varied to optimize the crystal structure and morphology. These composite membranes are perfectly selective to H_2, with permeability values approach and in fact exceed that of pure palladium. These findings demonstrate the potential of low cost group V

metals for H_2 separations with simultaneous carbon capture at temperatures compatible with the processes used for H_2 generation.

9:20am PS+TF-ThM5 Quantum Dot Sensitized Solar Cells using Nanoparticles of Si Compounds Fabricated by Multihollow Discharge Plasma CVD, *M. Shiratani, G. Uchida, M. Sato, Y. Wang, K. Koga, N. Itagaki*, Kyushu University, Japan

Quantum dot sensitized solar cells using semiconductor nano-particles have attracted much interest because they are expected to have a high efficiency and a low manufacturing cost. Narrow band-gap semiconductors such as CdS, PbS, and CdSe are employed as sensitizers, and they transfer photo-generated electrons in them to large band-gap semiconductors such as TiO2 under light excitation. Our interest has been concerned with quantum dot solar cells using Si coumpound nano-particles because Si is abundant and has little toxicity. We have succeeded in producing Si nano-particles of a narrow size dispersion using a multi-hollow discharge plasma CVD method [1], and have applied them to Si quantum dot sensitized solar cells [2]. In our CVD system, discharges were sustained in 8 small holes of 5 mm in diameter at SiH4 and H2 flow rates of 2 and 448 sccm. Si nano-particles were nucleated, grew in SiH$_4$/H$_2$ plasma produced inside small holes, and were transported to the downstream region by neutral gas flow. We also performed surface nitridation of Si nano-partciles to terminate dangling bond of the surface. Our experiments clearly demonstrated advantages of nitridation of Si nano-particles on the device performance; the short circuit current of Si QDs sensitized solar cells showed 1.3 times higher value by the nitridation and a photon to current conversion efficiency (PCE) achieved a high value of 40% at short wavelength of 350nm [3, 4]. Moreover, quantum dot sensitized solar cells using FeSi nanoparticles show better performance than those using Si nanoparticles. We will compare characteristics of three kinds of quantum dot sensitized solar cells using Si, Si/SiN core shell, and FeSi nanoparticles and discuss relationship between optical and electrical properties of the nanoparticles and the device performance.

[1] T. Kakeya, et al.: Thin Solid Films 506-507 (2006) 288.

[2] Y. Kawashima, et al.: Trans. Mater. Res. Soc. Jpn. 35 (2010) 597.

[3] G. Uchida, et al.: Phys. Status Solidi C, (2011) at press.

[4] G. Uchida, et al.: submitted to Jpn J. Appl. Phys.

9:40am PS+TF-ThM6 Structure of Organosilicon Polymeric Films Obtained by Expanding Thermal Plasma Chemical Vapor Deposition, *P.H. Tchoua Ngamou, M.C.M. van de Sanden, M. Creatore*, Eindhoven University of Technology, the Netherlands

Organosilicon polymeric thin films (SiCxHyOz) have attracted considerable interest due to their wide range of applications such as interlayers in gas/moisture diffusion multi-layer systems, low dielectric constant interconnect materials in microelectronic circuits and biocompatible coatings for medical implants, to name a few. An accurate control of the microstructure and composition of the films is generally required to meet specific requirements in the above-mentioned applications.

In this contribution, we report on the control of the composition and structure of films deposited in Ar/organosilicon precursor mixtures by using a remote plasma, i.e. the expanding thermal plasma, CVD process. The characterization of the deposited layers has been carried out by means of Fourier-transform infrared spectroscopy (FTIR), spectroscopic ellipsometry and X-ray photoelectron spectroscopy (XPS). The characterization of thin films showing a tunable chemical composition and optical properties has allowed identifying the main dissociation paths of the deposition precursor as controlled by the argon ions and electrons emanating from the plasma source, i.e. a cascaded arc, in the downstream region, where the monomer is injected. In particular, Ar ions are responsible for the charge exchange reaction with the monomer and electrons participate to the dissociative recombination with the molecular ions generated in the first reaction, as already proven in the case of other molecular gases [1]. An optimum in the monomer structure retention of 35 % has been observed under conditions of low plasma reactivity, i.e. high monomer flow-to-(Ar+,e-) flow rate ratio.

[1] M. Creatore, Y. Barrell, J. Benedikt, M.C.M. van de Sanden, Plasma Sources Science & Technology 15 (2006) 421-431.

10:40am PS+TF-ThM9 Impact of VUV Photons and Ions on Metal Oxide Films Prepared by Plasma-Assisted ALD with Substrate Biasing, *H.B. Profijt*, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The interest in plasma-assisted atomic layer deposition (ALD) has increased rapidly over the last

years, since it has been demonstrated that the presence of a plasma step can improve material

properties and ease processing conditions. Although it is known from other plasma-based techniques that

the photons and ions can play an important role during processing, their presence and influence have not

systematically been addressed so far for the specific case of plasma-assisted ALD. In this contribution,

we present a detailed investigation of the impact that VUV photons and energetic ions can have on the

properties of metal oxide thin films prepared by plasma-assisted ALD. We will demonstrate the

detrimental impact that VUV photons can have on electrical properties and we show that structural

material properties can be controlled by tuning the ion energy through substrate biasing. Optical

emission, retarding field energy analyzer, and Langmuir probe measurements were carried out in three

R&D plasma-assisted ALD reactors. In the O$_2$ plasmas employed, vacuum ultraviolet (VUV) photons with

energies up to 9.5 eV were detected and these photons were found to be able to generate electronic

defects at thin film interfaces. This was demonstrated by experiments in which Al$_2$O$_3$ passivated Si(100)

samples were exposed to O$_2$ plasmas. By exposing the samples through quartz and MgF$_2$ windows, the

role of ions was excluded and the specific role of the high energy VUV photons was confirmed

unambiguously. Furthermore, during regular ALD conditions, an ion energy of ~30 eV was measured.

This energy is sufficient to contribute to the ALD process by, e.g., the displacement of lattice atoms and

enhancement of the ALD surface reactions, however, it is low enough to prevent substantial damage to

the deposited layers. The impact of the ions was further explored by enhancing the energy of the ions

through the implementation of substrate biasing, either through substrate self-biasing or by RF biasing.

By enhancing the ion energy up to 230 eV, these experiments demonstrated that at 300°C the crystallinity

of TiO$_2$ films can be changed from the anatase to the rutile crystalline phase. Moreover, at a substrate

temperature of 200°C the rutile phase can be obtained when employing substrate biasing while normally

amorphous TiO$_2$ is obtained. These results are particularly significant as generally the deposition of rutile

TiO$_2$ is difficult to achieve by ALD due to substrate temperature limitations imposed by the precursors

used. It is therefore evident that substrate biasing is a promising method to extend the possibilities of ALD.

11:20am PS+TF-ThM11 Plasma Enhanced Atomic Layer Deposition and Plasma Etching of Gadolinium Oxide High-k Gate Dielectrics, *S.A. Vitale*, MIT Lincoln Laboratory, *C. Hodson*, Oxford Instruments Plasma Technology, UK

Lanthanide series oxides are being evaluated as second-generation high-k gate dielectric materials. In addition to improving transistor electrostatics by reducing the equivalent oxide thickness (EOT), using lanthanide series gate oxide capping layers allows the effective metal gate workfunctions to be tuned toward the silicon band edges, providing the correct transistor threshold voltages. However these non-traditional CMOS materials have several integration challenges that must be overcome, including depositing a thermally-stable, high quality film with low fixed charge and high-k,

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* Coburn & Winters Student Award Finalist

without damage to the underlying layers of the gate stack. In addition, in some gate-first and gate-last approaches, the oxide must be etched from the source/drain regions prior to silicidation.

In this work, plasma-enhanced atomic layer deposition (PE-ALD) of gadolinium oxide is reported for the first time. Using $Gd(iPrCp)_3$ as the organometallic precursor and a pure O_2 plasma as the oxygen source, Gd_2O_3 growth is observed from 150°C to 350°C, though the optical properties of the film improve at higher temperature. True layer-by-layer ALD growth of Gd_2O_3 does not occur under all conditions, in fact only a relatively narrow window of self-limiting ALD growth of 1.4 Å/cycle was observed at 250°C and below under certain precursor dose conditions. As the temperature increases, high-quality films are deposited, but the growth mechanism appears to become CVD-like. At 250°C, the refractive index of the film is stable at ~1.80 regardless of other deposition conditions, and the measured dispersion characteristics are comparable to those of bulk Gd_2O_3. The electrical characteristics of the films, such as fixed charge and dielectric constant, are extracted from C-V measurements using TiN metal gate capacitors, and will be reported.

The plasma etching rate of the ALD Gd_2O_3 film in a high-density helicon reactor is very low. Little difference is observed in etching rate between Cl_2 and pure Ar plasmas, suggesting that physical sputtering dominates the etching at high bias power. A threshold bias power exists below which etching does not occur, thus it may be possible to etch a metal gate material and stop easily on the Gd_2O_3 gate dielectric. The threshold bias power is lower in a Cl_2 plasma compared to an Ar plasma, which suggests there is a small ion-enhanced chemical component to the etching as well.

*This work is sponsored by the Department of the Air Force under Air Force Contract #FA8721-05-C-0002. Opinions, interpretations, conclusions and recommendations are those of the author and are not necessarily endorsed by the United States Government.

11:40am **PS+TF-ThM12 Nano- & Micro-Hybrid Materials by a Novel Plasma Deposition Method**, *M. Gulas, A. Felten,* Research Center in Physics of Matter and Radiation (PMR) Facultés Universitaires Notre-Dame de la Paix (FUNDP), Belgium, *A. Mansour, J. Guillot,* Centre de Recherche Public - Gabriel Lippmann, Luxembourg, *N. Claessens,* Universite Libre de Bruxelles, Belg
A novel low temperature plasma method using organometallic precursors has been tested and optimised to produce various hierarchical nano-hybrid and micro-hybrid materials. Very fast, operating at low or ambient temperature, this original "one pot" physical method is extremely simple, not requiring any pre- or post-treatment. The plasma-based technique can use any kind of electric discharge (direct current, radio or microwave frequency), does operate at low pressure or at the atmosphere, and can be combined with a large choice of plasma gases and organometallic precursors. Examples of the versatility of the method will be shown, including Pt and Ni-decorated carbon nanotubes (CNTs), Ag and Ti-decorated latex beads, and Pd-decorated clay sheets.

One focus of the presentation will be the preparation and full characterisation of bimetallic Pd/Rh - CNT hybrids. The x-ray diffraction (XRD) and TEM (EDX) analyses were used to confirm that the deposited nano-particles are indeed truly Pd/Rh bimetallic, excluding the possibility of a simple physical aggregate/mixture of the two metals ; complementary analytical tools such as x-ray photoelectron spectroscopy (global information) and scanning transmission x-ray microscopy (truly local information) reveal that the particles contain a metal/oxide ratio depending of the processing gas; they testify also of the possibility of a nano-particle core-shell structure and of a reorganisation of its structure depending of the processing gas.

Plasma Science and Technology Division
Room: 201 - Session PS-ThM

Neutral Beam and Low Damage Processing
Moderator: S. Bouchoule, CNRS-LPN

8:00am **PS-ThM1 2010 Plasma Prize Lecture - Super-low Damage Top-down Processing for Future Nanoscale Devices**, *S. Samukawa**, Tohoku University, Japan   **INVITED**
For the past 30 years, plasma process technology has led in the efforts to shrink the pattern size of ultralarge-scale integrated (ULSI) devices. However, inherent problems in the plasma processes, such as charge build-up and UV photon radiation, limit the process performance for nanoscale devices. To overcome these problems and fabricate nanoscale devices in practice, we have proposed damage-free neutral-beam process. In this

presentation, I introduce our developed damage-free etching, structure-designable deposition of super low-*k* SiOC film and low-temperature Si oxidation (thin SiO_2) processes using neutral beams and discuss the actual applications of neutral beam processing for future nanoscale devices (such as, Fin-MOSFET, and Quantum Dot Solar Cell). Neutral beams can perform atomically damage-free etching, deposition and surface modification. Then, the neutral beam process can precisely control the atomic layer chemical reaction and defect generation. This technique is a promising candidate for the nano-fabrication technology in future nanoscale devices.

8:40am **PS-ThM3 A Numerical Simulation Method for Plasma-induced Damage Profile in SiO_2 Etching**, *N. Kuboi*, T. Tatsumi, S. Kobayashi, J. Komachi, M. Fukasawa, T. Kinoshita, H. Ansai, Sony Corporation, Japan
To create high performance metal-oxide semiconductor devices, it is necessary to reduce variations in the critical dimension, the etching profile, and the amount of damage caused. Recent advancements in plasma processing for the gate electrode, sidewall, and high aspect contact hole have highlighted the importance of fully understanding how plasma induces damage and how to control this damage. We also need to find a way to quantitatively predict the damage depth profile using a numerical simulation that takes a realistic surface reaction into consideration, because it is quite difficult to observe the distribution of damage in the patterns with high aspect ratios. One commonly used simulation method, molecular dynamics (MD) calculation, unfortunately has a very limited range and cannot simultaneously consider a time-dependent etching profile in the 100 nm scale.

We developed a numerical simulation method for the distribution of plasma-induced physical damage to the SiO_2 and Si layers during fluorocarbon plasma ($C_4F_8/O_2/Ar$) etching. In our method, the surface layer is assumed to consist of two layers: a C-F polymer layer and a reactive layer. Physical and chemical reactions in the reactive layer divided into several thin slabs and in the deposited C-F polymer layer, which depends on etching processes are considered in detail considering reactivity of radicals, dangling bonds ratio, and generation of by-products (CF_2, SiF_2, and SiF_4) with ion energy dependence. As for ion and radical fluxes, we used the results from our previous experiments.

We used our simulation method to calculate the SiO_2 etch rate, the thickness of the C-F polymer layer (T_{C-F}), the selectivity of SiO_2 to Si layer, and the O_2 dependence of both the SiO_2 etch rate and the selectivity during $C_4F_8/O_2/Ar$ plasma etching in the steady state. Results demonstrated that calculation of the absolute values as well as their behaviors were consistent with those of our experimental data. We also successfully predicted depth profiles of physical damage to the Si and SiO_2 layers in the steady state introducing our re-gridding method, which were affected by the T_{C-F} value. When we calculated the time-dependence of the amount of Si damage, we found that much of the damage was generated in the pre- and early stages of the over etching step during the SiO_2/Si layer etching, in spite of the high selectivity. After that, the amount of damage was gradually decreased by etching and finally became constant.

These results demonstrate that the T_{C-F} value and the over etching time must be carefully controlled by process parameters to reduce the amount of damage during fluorocarbon plasma etching.

9:00am **PS-ThM4 Theoretical Analysis of Electron Transfer during the Process of Neutral Beam Generation**, *N. Watanabe*, S. Ohtsuka, T. Iwasaki, K. Ono, Y. Iriye, Mizuho Information & Research Institute, Inc., Japan, *S. Ueki,* BEANS Project 3D BEANS Center, Japan, *O. Nukaga,* Fujikura Ltd.,Japan, *T. Kubota,* Tohoku University, Japan, *M. Sugiyama,* University of Tokyo, Japan, *S. Samukawa,* Tohoku University, Japan
We have developed numerical simulation software named QuickQD[1,2] that calculates the time-evolution of wave functions of electrons based on the First pinciples Quantum Mechanics. We have applied QuickQD for analyzing neutral-beam generated by the neutral-beam etching system developed by Samukawa, et al [3]. Positive or negative ions passing through a graphite aperture of this etching system are converted to neutral atoms by exchanging their valence electrons during a collision with the aperture sidewall.

Our numerical model consists of an ion (Cl- or Cl2+) and 24 carbon atoms forming a graphite sheet. The ion has been moved to collide with the graphite sheet and then bounce back to its original position. QuickQD has simulated the time-evolution of several ten wavefunctions of both the ion and carbon electrons during the whole process of the collision. We have evaluated the distribution of electron density around the ion, and we have determined the probability of neutralization.

We have obtained some numerical results that agree well with experiment results, for example,

a negative Cl- ion transfers its valence electrons to the graphite and is converted to a neutral Cl atom with high probability, meanwhile a positive Cl2+ ion receives valence electrons from the graphite and is converted to a neutral Cl2 molecule with low probability[4].

To understand the quantum process of electron transfer and the difference of neutralization efficiencies between a negative ion and a positive ion, we have investigated the behavior of each time-evolving electron wave function. We have found that some electrons that existed in the orbital of Cl- before the collision were mainly transferred after the collision to some orbitals of graphite whose orbital energies were close, namely, resonant transitions whose transition rates are relatively high. Meanwhile, some electrons that existed in the orbitals of graphite before collision of Cl2+ were transferred after the collision to the orbital of Cl2+ whose orbital energies were not close, namely, Aujer like complicated transitions, whose transition rates are relatively low.

In this talk, we will show the time-evolution of wave functions based on the First pinciples Quantum Mechinics, which simulated the neutralization processes that occured in the neutral beam etching system.

[1] N. Watanabe and M. Tsukada, Phys. Rev. E. 65 036705 (2002).

[2] http://www.mizuho-ir.co.jp/solution/research/semiconductor/nano/meso

[3] S. Samukawa et al., Jpn. J. Appl. Phys., 40, L779 (2001).

[4] T. Kubota, N. Watanabe, et al., J. Phys. D. 44 125203 (2011)

9:20am PS-ThM5 Energy and Angular Distribution Analysis for Neutral Beam and Application for Etching Simulation, *S. Ohtsuka*, *N. Watanabe, T. Iwasaki, K. Ono,* Mizuho Information & Research Institute, Inc., Japan, *Y. Iriye, O. Nukaga, S. Ueki,* BEANS Project 3D BEANS Center, Japan, *T. Kubota,* Tohoku University, Japan, *M. Sugiyama,* University of Tokyo, Japan, *S. Samukawa,* Tohoku University, Japan

The neutral-beam etching system developed by Samukawa et al [1] has a carbon plate which has numerous apertures, where positive or negative ions pass through. In this system, most of those ions passing through the apertures are efficiently converted into neutral atoms. We consider ions are neutralized by the collision with aperture sidewall. A negative ion transfers some of their valence electrons to the aperture sidewall by the collision, and a positive ion receives some valence electrons from the aperture sidewall. The dynamical process of electron transfer by the collision can be described by the Quantum Mechanics as a time-evolution of wave-function during the collision, and we have developed computational simulation software named QuickQD [2].

To realize more practical neutral-beam etching system, we also have to analyze the energy and angular distribution passing through the aperture. Those distributions characterize the ability of etching system. In other words, to achieve efficient etching system, we have to develop optimized aperture configurations (i.e. arrangement and aspect ratio of apertures) and get conditions for suitable energy and angular distribution of neutral beam.

In this study, we calculate the trajectory of particles generated by Monte-Carlo method, and analyze the energy and angular distribution of neutral beam at aperture outlet. To analyze energy and angular distribution at outlet, we have to determine the initial conditions of incident beam at aperture inlet, and have to describe the scattering process for collision between incident particles and side wall of aperture. We determine initial beam condition at inlet using the experimental data fitting. And we use the inelastic surface scattering model known as Hard-Cube model [3] for treating collision between particles and side wall of aperture. Particles injecting into aperture which have broad angular distribution are collimated by this inelastic scattering process.

Using above simulation scheme, we analyze the energy and angular distribution for specific aperture configuration (i.e. aperture aspect ratio) and compare with experimental data. We also analyze the particle distribution of neutral beam at silicon wafer injecting from aperture outlet and discuss the uniformity of neutral beam etching. Using above angular distribution of neutral beam and etching simulator, we predict etching shape by neutral beam generated by various aperture configurations (i.e. aperture aspect ratios).

[1] S. Samukawa et al., Jpn. J. Appl. Phys., 40, L779 (2001).

[2] N. Watanabe and M. Tsukada, Phys. Rev. E. 65 036705 (2002).

[3] R. M. Logan and R. E. Stickney, J. Chem. Phys., 44, 195 (1966).

9:40am PS-ThM6 High-Aspect-Ratio Silicon Etching using Large-Diameter Neutral Beam Source, *T. Kubota*, Tohoku University and BEANS Project, Japan, *A. Wada,* Tohoku University, Japan, *S. Ohtsuka, K. Ono,* Mizuho Information & Research Institute, Inc., Japan, *H. Ohtake,* Tohoku University, Japan, *S. Ueki, Y. Nishimori,* BEANS Project, Japan, *G. Hashiguchi,* Shizuoka University and BEANS Project, Japan, *S. Samukawa,* Tohoku University, Japan

Plasma etching is widely used for fabricating semiconductor electronic devices and microelectromechanical systems (MEMS), but plasma etching is known to cause damages due to the charge-up and UV irradiation. To overcome plasma-induced damages, we have developed a neutral beam source with very high neutralization efficiency. The neutral beam source achieved high neutralization efficiency by using negative ions from pulse-time modulation plasma, and UV irradiation was drastically reduced. To apply this neutral beam source to mass production, we have developed a large-diameter neutral beam (NB) source by using an 8-inch-diameter inductively coupled plasma etcher (Panasonic Factory Solutions Co., Ltd. E620) as an ion source. In the previous study, the beam flux of argon NB was more than 1 mA/cm2 in equivalent current density and the neutralization efficiency was more than 99%. Vertical Si etching using F_2 gas chemistry was also achieved. Also, beam was successfully accelerated by bias applied to the aperture plate [1].

In this study we investigated high-aspect-ratio silicon etching. At first, angular distribution of NB was measured. As a result, Gauss-function-like distribution was observed and the width of the distribution was determined by aspect ratio of the aperture. On the other hands, angular distribution of incoming ions from plasma to the aperture was almost uniform. Also, plasma parameters such as source power and gas flow rate did not affect the distribution. From these results, it is supposed that aperture plays a dominating role in generation of collimated NB. Then, silicon etching by chlorine (Cl_2) NB was performed using apertures with aspect ratio of 10 and 20. By using the aperture with aspect ratio of 10, almost vertical sidewall with a slight positive taper of 6 degree was achieved. The aperture with aspect ratio of 20 led to almost vertical etching. Silicon trench etching with aspect ratio of about 22 was achieved using the aperture and chlorine NB.

[1] T. Kubota et al., J. Vac. Sci. Technol. A 28(5), 1169 (2010).

10:40am PS-ThM9 Improvement in the Evaluation Technique for Plasma-Etch Si Damage using Photoreflectance Spectroscopy with Temperature Control, *A. Matsuda, Y. Nakakubo, Y. Takao, K. Eriguchi, K. Ono*, Kyoto University, Japan

In etching processes during MOSFET fabrication, bombardment of high-energy ions from plasma creates damaged structures in layers near the substrate surface, characterized by defect sites in the crystalline structure such as vacancies, interstitials, displacements, and dangling bonds. The negative effects of the damage on device characteristics (such as drain current degradation) have become increasingly significant as devices scale down rapidly [1]. To realize low-damage process, an advanced damage evaluation technique is essential. Photoreflectance spectroscopy (PRS) is an optical technique capable of detecting damage with high sensitivity. The surface is perturbed with an electric field by a modulation laser beam, and the reflectivity of a probe beam is measured. PRS has been studied as an advanced technique for contactless damage evaluation.

In this study, we employed an improved technique, where the temperature of the sample is controlled with liquid N_2 during PRS measurement. N-type Si (100) wafers were exposed to an inductively coupled plasma using argon gas, under various rf-bias powers to control the incident ion energies (E_i). At room temperature, the amplitude of the spectral peak decreased with the increase in E_i. This feature is explained in earlier literature that carriers trapped at defect sites lower the surface potential (V_s), resulting in a decrease of the amplitude [2]. Over $E_i \approx 400$ eV, the peak became smaller than background fluctuation, rendering quantitative characterization impossible. When the sample was cooled to 90 K, the spectra were enhanced and the peak of the high-E_i sample was revealed. By fitting the spectra to a functional form [3] and modeling the parameters' temperature dependences, we found that the amplitude enhancement is related to the temperature dependence of the spectral broadening parameter (Γ). We also found that, at a fixed temperature, Γ for damaged surfaces were larger than that of the control sample. These results show that the damage causes changes in V_s and Γ, but by controlling the sample temperature, we were able to lower Γ, which increased the amplitude and revealed the peak.

The PRS-based damage evaluation technique discussed here expands the range of the applicable plasma damage conditions. Furthermore,

temperature dependences of the spectra and its parameters (*e.g.* Γ and/or optical band gap) give us an insight into the band structures of damaged Si. This PRS-based technique is expected to be potentially useful as a future *in-situ* monitoring technique.

[1] K. Eriguchi *et al.*, IEDM Tech. Dig., 2008, p. 436

[2] H. Wada *et al.*, J. Appl. Phys. **88**, 2336 (2000)

[3] D. E. Aspnes, Surf. Sci. **37**, 418 (1973)

11:00am PS-ThM10 The Mechanism of Thin SiO₂ and GeO₂ Film Formation during Low-Temperature Neutral Beam Oxidation Process, *A. Wada,* Tohoku University, Japan*, K. Endo, M. Masahara,* AIST, Japan*, S. Samukawa,* Tohoku University, Japan

The thermal oxidation process is usually used to form the gate dielectric films of MOSFETs. However, it involves high temperatures (usually > 800°C), which causes problems. For example, after using the high-temperature oxidation process to form SiO_2 films, residual compression stress between the Si substrate and SiO_2 remains due to the difference in the thermal expansion coefficient between Si and SiO_2. This residual stress degrades the sub-threshold characteristics of MOSFETs because it increases interfacial state density. Especially, in case of future 3-dimensional transistors such as FinFETs, stress concentration occurs at corner and edge of 3D structures, which may cause drastic increase of leakage current. There have been recent active investigations on the thermal oxidation of Ge to enable the fabrication of high-mobility Ge MOS transistors. After high-temperature thermal processes, however, Ge oxide has poor thermal stability and a large amount of suboxide.

We developed an alternative oxidation process to solve these problems using a low temperature neutral beam (NB) technique to form the gate dielectric film. In this study, we investigated the mechanism to form thin oxide films using a low-temperature neutral beam oxidation (NBO) process. Arrhenius plot has shown that activation energy of NBO was extremely low, which enabled low-temperature oxidation at 300°C or even at room temperature. This should be because bombardment energy of oxygen beam assisted the oxidation reaction. Also, we investigated that the suboxide in thin oxide film using NBO process. As a result, there was little suboxide at the interface between oxide films and semiconductor using NBO process even at low-temperature. These results demonstrate the outstanding potential of the low-temperature NBO process for fabricating gate dielectric films.

11:20am PS-ThM11 Room Temperature Radical Annealing of Plasma Damaged Gallium Nitride, *S. Chen*, Y. Lu, K. Takeda, K. Ishikawa, H. Kondo,* Nagoya University, Japan*, H. Kano,* NU Eco-engineering Co., Ltd, Japan*, H. Amano,* Nagoya University, Japan*, Y. Tokuda,* Aichi Insititute of Technology, Japan*, T. Egawa,* Nagoya Institute of Technology, Japan*, M. Sekine, M. Hori,* Nagoya University, Japan

This paper reports an attempt of low-temperature recovery for gallium nitride (GaN) damaged by the exposure of a chlorine-based etching plasma. The work is motivated by the challenge for manufacturing highly-reliable GaN based devices which have a great deal of potential in optical, high-frequency, and high-power electronics field. So far, high temperature annealing or nitrogen plasma were used as the post-process. However, the high-temperature treatment could not restore the reduced atomic ratio of nitrogen on the damaged surface. The nitrogen plasma introduces damage by the ion bombardment. In this study, a high-density radical anneling in room temperature was newly proposed and evaluated in all in-situ experimental system consisted of etching, radical annealing, and surface analysis.

Radicals and ions extracted from a chlorine plasma were irradiated to n-GaN with an ion dose of 5 x 1016cm-2 at 500 eV [1]. Then the radical annealing using nitrogen radical (N*) or hydrogen radical (H*) with a radical dose of 1 x 1018cm-2was applied using a high-density radical source [2] at room temperature. The X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) evaluation carried out after each process.

In N* annealing case, the surface chloride was removed and N/Ga was improved, but there was no change in the composition ratio of oxygen (O). On the other hand, hydrogen radical (H*) could efficiently remove O, and N/Ga was improved greatly. Other characteristic findings were that Ga-Ga (metallic Ga) was observed in the Ga 3d spectra and the surface roughness increased from 0.335 to 0.646 nm rms.

As a result, the radical annealing at room temperature was shown to be very effective for improving GaN stoichiometry to achieve a better interface, whereas the condition should be optimized very carefully.

[1] S. Chen, et al., Proc. 63rd GEC/7th ICRP (Paris, 2010), BT1-005.

[2] S. Chen, et al., Jpn. J. Appl. Phys. 50, 01AE03 (2011).

11:40am PS-ThM12 Effect of Rapid Thermal Annealing on Si Surface Damage by HBr/O₂- and H₂-Plasma, *Y. Nakakubo, A. Matsuda,* Kyoto University, Japan*, M. Fukasawa,* Sony Corporation, Japan*, Y. Takao,* Kyoto University, Japan*, T. Tatsumi,* Sony Corporation, Japan*, K. Eriguchi, K. Ono,* Kyoto University, Japan

Plasma-induced Si substrate damage has become one of the critical issues in advanced MOSFETs with shallower junction in source/drain extension (SDE) regions, since the damaged layer thickness will be in conflict with the device design margin (e.g. ~ 5 nm in 32-nm technology node). This damage causes the device performance degradation by forming Si loss (Si recess structure) [1]. Ohchi et al. have reported that the damaged layer by hydrogen-containing plasma is thicker than that by plasma without hydrogen, resulting in deeper Si recess [2]. Eliminating the damaged layer by wet etch and reconstructing the crystalline structure by thermal processes are strongly required, but there have been few studies on these issues. In this study, we report the effect of rapid thermal annealing on the damaged layer by HBr/O₂- and H₂- plasmas.

P-type silicon substrates with thermal-oxide layer (2 nm) were exposed to the capacitively coupled plasma (CCP) by applying a dual bias frequency (60/13.56 MHz). HBr/O₂ and H₂ gases were used. Damaged samples were cleaned by the dilute-HF solution (DHF) for 2 min before rapid thermal annealing (RTA) at 1035 °C for 10 s in a N₂ gas ambient. The structure and the electrical conductivity were identified using spectroscopic ellipsometry (SE) and current-voltage (I-V) measurement, respectively. Capacitance-voltage (C-V) method was performed to analyze the features of the defect site in the damage samples.

Although all the damaged samples after RTA had a thicker oxide layer (~ 1.4 nm) compared with that of the native oxide layer (~ 0.6 nm) grown on the Si surface treated by SC2, a much higher current through the thick oxide (~ 20 mA at -0.1 V) was observed in comparison with that through the native oxide (~ 0.7 mA at -0.1 V). This feature is due to the nitrided Si that may be assigned by SE. This nitirided layer was found to be difficult to remove (etch) even by the DHF-treatment of several minutes, and thus the damaged MOSFETs may suffer from performance degradation by the presence of the nitrided layer. These findings imply that in the case of H-plasma, the process recipe for RTA targeted to cure the plasma-induced Si damage should be carefully optimized.

[1] K. Eriguchi *et al.*: IEEE Electron Dev. Lett. **30** (2009) 712.

[2] T. Ohchi *et al.*: Jpn. J. Appl. Phys. **47** (2008) 5324.

* Coburn & Winters Student Award Finalist

Thursday Afternoon, November 3, 2011

Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films
Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics**, *D. Levi*, National Renewable Energy Laboratory **INVITED**
With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has lead to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of $1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

2:40pm **EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films**, *N.J. Podraza*, University of Toledo
Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or "nanocrystalline" silicon (nc-Si:H) absorber layers, although the best "nanocrystalline" absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract ε for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining ε and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate ε for the component materials may be obtained. This works seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in ε, and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze

structurally graded thin films under different material and measurement circumstances.

3:00pm **EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of Cu(In,Ga)Se$_2$ Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process**, *D. Attygalle*, University of Toledo, *V. Ranjan*, Old Dominion University, *P. Aryal*, University of Toledo, *S. Marsillac*, Old Dominion University, *R.W. Collins*, University of Toledo
With record efficiencies above 20%, Cu(In,Ga)Se$_2$ (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of $(In_x,Ga_{1-x})_2Se_3$. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in (ψ, Δ) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of $(In_x,Ga_{1-x})_2Se_3$ to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid $Cu_{2-x}Se$ phase is believed to form on top of a bulk layer consisting of mixed phases of Cu(In,Ga)Se$_2$ and $Cu_{2-x}Se$ [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed (ψ, Δ) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top $Cu_{2-x}Se$ phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the (ψ, Δ) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "Cu(In,Ga)Se$_2$ Thin-film evolution during growth from (In,Ga)$_2$Se$_3$ precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

3:40pm **EL+AS+EM+MS+PS+TF-ThA6 Bulk Hetrojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry**, *K. Uppireddi*, *L. Yan*, HORIBA Scientific
The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-buytric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

4:00pm **EL+AS+EM+MS+PS+TF-ThA7** , *N. Leick*, *J.W. Weber*, *M.J. Weber*, *A.J.M. Mackus*, *H.C.M. Knoops*, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands
The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and electrical properties of the films which is very relevant for their

applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd (1.00 ± 0.06 Å, 0.47 ± 0.04 Å, 0.14 ± 0.02 Å). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru: ρ_{SE} ~23 μΩ.cm and ρ_{FPP} ~16 μΩ.cm). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi *et al.*, Phys. Rev. B **74**, 205117 (2006)

4:20pm EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition, *D. Schmidt, N. Ianno, E. Schubert, **M. Schubert***, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle ($\theta_i =$ 85°) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports, *W. Ogieglo, N.E. Benes, **H. Wormeester***, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these supports can not be obtained from a direct inversion. The reason for this is

that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema Thin Solid Films **455-456**, 747-751 (2004)

5:00pm EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films, *M.A. Motyka, M.W. Horn*, Pennsylvania State University, *N.J. Podraza*, University of Toledo

Vanadium oxide (VO_x) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film (ρ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality VO_x may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to V_2O_5 and VO_2. The higher quality VO_x thin film material also has been observed via transmission electron microscopy (TEM) to contain VO/V_2O_3 nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting VO_x film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) can be obtained for these materials over the full spectral range. Differences in ε due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically, ε are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and ε are correlated with films exhibiting the desirable device electrical properties. In situ real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited VO_x thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was SiO_2 grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions, *D.W. Ferrara, **R.E. Marvel**, J. Nag, R.F. Haglund*, Vanderbilt University

Vanadium dioxide (VO_2) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally ($T_c = 68°C$), optically, or electrically. Recently, VO_2 films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of VO_2 can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of VO_2 as it undergoes the SMT; however, previous measurements of the optical constants of VO_2 reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of VO_2 were deposited on either silicon, glass, or sapphire substrates by pulsed

laser ablation of vanadium metal targets in 10 mTorr oxygen (O_2) background gas, followed by annealing at 450°C in 250 mTorr of O_2. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting VO_2, metallic VO_2, and vanadium pentoxide (V_2O_5). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of V_2O_5 to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

Plasma Science and Technology Division
Room: 202 - Session PS+SS-ThA

Plasma Surface Interactions (Fundamentals & Applications) II
Moderator: A. Kumar, Case Western Reserve University

2:00pm PS+SS-ThA1 Plasma Prize Lecture - The Role of Atomic Hydrogen on Plasma Synthesis of Carbon Nanotubes, *E.S. Aydil**, University of Minnesota **INVITED**
Hydrogen containing discharges are used widely in plasma synthesis of a variety of nanustructures including nanoparticles and carbon nanotubes. We developed a method for measuring the H-atom flux at the plane of the substrate surface during H_2 plasma exposure. Our method is based on infrared measurements of the change in free-electron absorption in a polycrystalline ZnO film when this film exposed to H atoms. Hydrogen acts as an electron donor in ZnO, and thus the concentration of hydrogen-generated free carriers can be extracted from their absorption in the infrared. The change in the concentration of free carriers can in turn be related to the flux of H atoms impinging on a ZnO film placed on the substrate platen. Using this and a suite of additional plasma and material characterization techniques, including optical emission, infrared, and Raman spectroscopy and electron microscopy we systematically investigated the interrelation among plasma gas phase composition, catalysts morphology, catalyst structure, and carbon nanotube structure in plasma enhanced chemical vapor deposition of carbon nanotubes. The structures of carbon nanotubes grown from catalytic nanoparticles via PECVD in CH_4 /H_2 mixtures show a strong dependence on the H_2-to-CH_4 ratio in the feed gas. Hydrogen plays a critical role in determining the final carbon nanotube structure through its effect on the catalyst crystal structure and morphology. At low H_2-to-CH_4 ratios, iron catalyst nanoparticles are converted to Fe3C and well-graphitized nanotubes grow from elongated Fe_3C nanoparticles. High H_2-to-CH_4 ratios in the feed gas result in high atomic hydrogen concentrations in the plasma and strongly reducing conditions, which prevents conversion of Fe to Fe_3C. In the latter case, poorly-graphitized nanofibers grow from ductile bcc iron nanocrystals that are easily deformed into tapered nanocrystals that yield nanotubes with thick walls. In the limit of pure hydrogen the cylindrical graphene walls of a nanotube are etched and amorphized by the H atoms. Etching is not uniform across the length of the CNT but rather, small etch pits form at defective sites on the CNT walls along the entire nanotube length. Once an etch pit is formed, etching proceeds rapidly, and the remainder of the CNT is quickly etched away.

2:40pm PS+SS-ThA3 CF and CF_2 Contributions to Plasma-Enhanced Chemical Vapor Deposition of Fluorocarbon Films in C_xF_y Systems, *M.F. Cuddy, E.R. Fisher*, Colorado State University
Inductively coupled fluorocarbon (FC) plasmas produced from C_xF_y ($x,y \geq$ 1) precursors are widely employed in industrial processes ranging from circuitry fabrication to preparation of low-*k* optical coatings. The utility of the plasma system is largely dictated by the y/x ratio, specifically in that precursors with lower ratios tend to more efficiently deposit FC films. Film growth is thought to be related to the behavior of radical species within the plasma, such as CF and CF_2. We report here on gas-phase behavior of these radicals in FC plasma systems with precursor y/x ratios $\leq$ 4, including relative gas-phase concentrations and kinetics and subsequent contributions to Si wafer processing. Our imaging of radicals interacting with surfaces (IRIS) experiment reveals that the propensity for scatter of CF and CF_2

declines dramatically with decreases in precursor y/x ratio. Similarly, with decreasing y/x ratios, we observe increases in FC film surface energies, suggesting that avenues to tailor specific film properties are feasible. High-resolution x-ray photoelectron spectra and surface sum frequency vibrational spectra which corroborate the relationship between the choice of precursor and characteristics of deposited FC films will also be discussed. Ultimately, this work aims to establish a connection between species behavior near surfaces and resulting film properties during FC plasma processing.

3:00pm PS+SS-ThA4 Polymer Surface Modification: Real-time In Situ Electron Spin Resonance Study for Plasma Processes, *K. Ishikawa, N. Sumi*, Nagoya University, Japan, *A. Kono, H. Horibe*, Kanazawa Institute of Technology, Japan, *K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan
A comprehensive understanding of interaction between plasmas and soft-materials is essential for advanced plasma processing technology. Simultaneous measurements of the gas-phase ESR signals and the surface dangling bond signal [1,2], and kinetics analysis of radical formation were performed using *in situ* real-time electron spin resonance (ESR). Chemical reactions under plasma are very complicated, due to the simultaneous irradiation of electrons, ions, radicals, and photons. Therefore, the individual contributions of each of these reactive species in the plasma must be elucidated.

An ESR system was connected to a plasma discharge system (2.45 GHz, 50 W) using a quartz tube with an inner diameter of approximately 9 mm. Gas (H_2, O_2, etc.) was flowed into the quartz tube and the pressure was maintained at approximately 10 Pa in the down-flow region. ESR measurements were conducted using a standard X-band (9 GHz) spectrometer (Bruker Biospin, EMX plus) with a microwave resonator. The quartz tube and polymer (PTFE, PMMA, etc.) film sample were inserted inside the ESR cavity in the down-flow region, typically 20 cm from the plasma discharge.

Individual contributions from gaseous radicals and plasma emission light have been studied in a similar manner using pallets for plasma process evaluation (PAPE) [3].

For irradiation with both atomic H and VUV on the PTFE film, significant acceleration in the rate of C-DB formation was observed at the beginning of irradiation.

Moreover, the surface radicals produced immediately changed to peroxy-radicals when the treated PTFE films were exposed to air. This suggests high reactivity of C-DB with oxygen and the peroxy-radical species can contribute to enhancement of the surface biocompatibility.

In summary, during exposure of gaseous radicals on the polymer surface, the *in situ* real-time ESR technique was demonstrated as a new experimental approach to the microscopic understanding of chemical reactions on surfaces with gaseous radicals during plasma processes. We have successfully obtained information regarding the reaction mechanism with radicals generated by plasma induced surface interactions.

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[2] K. Ishikawa, *et al*., Appl. Phys. Lett. 81, 1773-1175 (2002).
[3] S. Uchida, *et al*., J. Appl. Phys. 103, 073303:1-5 (2008).

3:40pm PS+SS-ThA6 Control of Hydrocarbon Surface Density during H_2/D_2/Ar Low Temperature Plasma Interaction, *N. Fox-Lyon, G.S. Oehrlein*, University of Maryland, College Park, *N. Ning, D.B. Graves*, University of California, Berkeley
Control of surface properties of hydrocarbon materials during interaction with H_2/D_2/Ar low temperature plasma has applications in diverse areas including: thin film synthesis, electronic device manufacturing, nuclear fusion reactor design, and plasma sterilization. Plasma processing/exposure of hydrocarbon materials can cause large changes to the surface chemistry and morphology due to interaction with ions, reactive neutrals, and UV/VUV photons. Hard hydrocarbon materials such as amorphous hydrocarbon (a-C:H) and diamond-like carbon (DLC), suffer a loss of density and a thick modified layer with reactive plasma etching through reactant saturation of the surface and an increase in density and formation of a thin modified layer by inert plasma etching through selective sputtering of H, whereas soft hydrocarbon materials (polymers, biomaterials) exposed to reactive and inert plasmas have been shown to increase in density and become chemically modified. In this work we have explored the plasma/surface interaction with hard/soft hydrocarbon films using different

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* 2009 Plasma Prize Winner

$H_2/D_2/Ar$ gas feedstock compositions along with different ion energy/fluence to the surface. The time dependent changes in optical properties and the etch yields were found using real time in-situ ellipsometry. Using multilayer films (e.g., soft a-C:H over hard a-C:H) we monitored dynamic changes in the penetration/modification depths for different plasma chemistries.

Shallow modifications by inert plasmas (such as Ar) are well understood. Ar plasma depletes H from the surface of a-C:H films through selective sputtering, scaling with ion energy. H_2 plasmas have been shown to cause deep hydrogenation of the surface not predicted with TRIM models. Mixing the processing gas (Ar/H_2) can be used to control the surface density from H depleted to H saturated. To better understand the roles of ion mass, etch rate and diffusion on the depth/degree of modification seen for H_2 plasmas, we performed comparable studies using D_2. We find that increasing the mass of the ions (by using H isotopes such as D) causes a large change in the etching and surface modification behavior. The etch rate of hard a-C:H in D_2 plasma is ~2 times the rate in H_2 plasma, and surfaces show a lower degree of modification (hydrogenation) than for H_2 plasma. In soft hydrocarbon materials exposed to D_2, H_2, and Ar plasmas (listed in order of modification, least to greatest), we find that the density increase is dependent on the ion chemistry, energy, penetration depth, and mass. The data will be compared with molecular dynamics simulation results.

4:00pm PS+SS-ThA7 Atomic Force Microscopy Determination of the Elastic Modulus of Nanometer Thick, Ultra-Stiff Modified Layers after Plasma Etching of a Polymer Film, *T. Lin,* University of Maryland, College Park*, H.C. Kan,* National Chung Cheng University, Taiwan, Republic of China*, R.L. Bruce, G.S. Oehrlein, R.J. Phaneuf*, University of Maryland, College Park

We report on a determination of the elastic modulus for ultrathin (< 2nm) stiff damaged layers produced by argon plasma etching of the model photoresist polymer, polystyrene (PS). Measured force curves allow a direct determination of the effective modulus of the damaged layer plus polystyrene underlayer within a model which accounts for adhesive forces. The modulus of the modified layer is then extracted via comparison with numerical simulations for contact between a spherical AFM probe and a bilayer-structured film system in a Hertzian mechanics model. Our results show directly that an extremely stiff modified layer is formed, with the modulus increasing with Ar-ion energy during etching, in good quantitative agreement with estimations based upon measurement of the dominant corrugation wavelength and buckling theory.

4:20pm PS+SS-ThA8 Polymer Hardening Technique for Enhancement in Etch Selectivity/Durability Using DC Superimposed Capacitively-Coupled Plasma, *S. Okamoto, A. Nakagawa, F. Inoue, H. Oka,* Tokyo Electron Miyagi Ltd., Japan*, H. Mochiki, K. Yatsuda*, Tokyo Electron Ltd., Japan

Higher aspect ratio of DRAM capacitor is required in order to maintain enough capacitance as the device structure is scaled down. The electrode of DRAM capacitor is generated in mold by metal CVD – typically TiN, and the mold is fabricated by RIE – typically dielectric. Thus, it is necessary to develop new techniques to fabricate higher aspect ratio dielectric mold for further DRAM scaling. RIE challenges for mold fabrication are high dielectric etch selectivity to mask, minimum bowing, and sustainment of enough bottom CD.

Generally speaking, mold etch process is optimized by accurate polymer control. However, conventional polymer control technique became marginal in highly scaled DRAM structure. Even slightly excessive polymer makes bottom CD smaller, and sometimes clogs the top portion of mold. On the other hand, slightly lacking polymer bridges neighboring molds at the top and/or sidewall portion due to lack of etch selectivity to mask and/or bowed etch profile.

In this paper, we suggest DC superimposed capacitively-coupled plasma (CCP) etch technique as a breakthrough of high aspect ratio dielectric etch. High energetic electrons emitted and accelerated by superimposed DC harden the polymer generated on mask and sidewall. This hardening technique works in two roles. The first role is etch selectivity enhancement of undesired etch material. Since polymer is maintained thin enough with good etch selectivity to mask, the top portion of mold is not clogged by polymer. The second role is etch durability enhancement of undesired etch portion. Normally, ultra high aspect ratio dielectric etch needs very high ion energy, which results in bowing etch profile due to incoming angular ions. But, superimposed DC hardens the sidewall polymer, and prevents etch profile from bowing. Bottom CD can be enlarged in the over etch step after etch front reaches etch stop layer. In general, bowing etch profile becomes significant during the over etch step. However, this effect can be avoided with stiff polymer enhanced by superimposed DC.

In conclusion, etch selectivity/durability of the undesired etch material/portion can be enhanced by superimposed DC as long as polymer

is generated in the desired area by etch process optimization. Superimposed DC allows us to enhance etch selectivity/durability not with thickness of polymer but stiffness of polymer.

4:40pm PS+SS-ThA9 H$_2$O Plasma Surface Modification of Track-Etched Polycarbonate Membranes Leading to Polar Surface Functionalization and Improved Wettability, *B.D. Tompkins, J.M. Dennison, E.R. Fisher*, Colorado State University

Plasma surface modifications have the ability to improve performance and realize new applications for polymer membranes in a variety of areas including: microfiltration, gas separation, and water treatment. Past studies in our labs have shown that although some polymer membranes can be successfully modified and are stable after treatment, many partially revert to their untreated state when aged. We are developing a technique that utilizes inductively coupled H_2O plasmas to implant polar functional groups onto the surface of track-etched polycarbonate membranes free of wetting agents. Water contact angle results on freshly treated and aged membrane samples show that the treated membranes have improved wettability compared to untreated samples and that the effects persist after treatment. Analysis of freshly treated samples using x-ray photoelectron spectroscopy (XPS) shows increases in oxygen incorporation, whereas high resolution XPS spectra of the C1s region shows that the fundamental polycarbonate structure is maintained near the surface. Treatment effectiveness under different plasma conditions, aqueous flux used to evaluate the performance of modified membranes, analysis of gas phase plasma species using optical emission spectroscopy (OES) to probe the processes that lead to surface modification, and a comparison with a similar plasma system using a mixture of O_2 and NH_3 as feedgasses will be discussed along with comparisons to other polymer membrane materials treated under similar conditions.

5:00pm PS+SS-ThA10 Plasma Printing: A New Inline Technology for Polymers Surface Modification, *E.A.D. Carbone, M.W.G.M. Verhoeven,* Eindhoven University of Technology, Netherlands*, W.J.M. Brok, A. Stevens,* Innophysics B.V., Netherlands*, J.J.A.M. van der Mullen*, Eindhoven University of Technology, Netherlands

Fast and easy tunable patterning of surfaces has become of growing interest in the last couple of years in different fields like surface functionalization, thin film coatings and biomedical applications.

The concept of *Plasma Printing* combines the advantages given by the non-equilibrium character of pulsed corona discharges (tunability of surface chemistry), their creation and propagation along small volumes (local plasma treatment) and the mobility of the plasma source as a conventional printer (inline processing). This unique combination allows to treat (in real time) surfaces with arbitrary patterns design with limited restrictions unlike in the use of atmospheric pressure (dielectric barrier discharge) DBD for patterning of surface (also called DBD stamping).

InnoPhysics developed a proprietary Digital-on-Demand PlasmaPrint hardware solution that enables software patterned surface functionalization, etching and deposition of functional coatings on thin (plastic) substrates. A few kV sinusoidal pulse is applied on the electrode gap (pin to plate geometry configuration) in the 50-100 kHz range which generates a 1-10 μs pulsed plasma of about ~ 200 μm diameter in contact with the surface.

In order to assess the performances of the setup, a parametric study of polymers with respect to gas mixtures was performed to detect optimum of surface hydrophilization as well as selective chemistry groups grafting like OH, NH and CO.

PE, PET, FEP as well as PTFE (and PCTFE) were treated by nitrogen and different admixtures of gas/solution namely oxygen, ethanol, water and ammonia (NH_4OH solution). The surfaces were analyzed by water contact angle (WCA), X-ray photoelectron spectroscopy (XPS) and IR spectroscopy in attenuated total reflectance mode (FTIR ATR).

WCA was used to measure the surface energy of the surface and significant improvements of wetting properties were found for a few seconds of treatment time (i.e. <30° in the case of PET treated by N_2/NH_3). Grafting of N species up to a few percents was also found for various plasma compositions. The deconvolution of high resolution C1s, N1s and O1s spectra combined with the analysis of the IR spectra for the same conditions allowed eventually to get more insight in the chemical groups grafting at the surface following the plasma treatment.

5:20pm PS+SS-ThA11 Design of a Plasma Cleaning Unit to Clean Backside Contamination on Substrates, *F.T. Molkenboer, N.B. Koster, A.J. De Jong, J.C.J. van der Donck, A.M.C.P. de Jong, O. Kievit*, TNO, Netherlands

In this presentation we will report our work on the design and experimental results of a plasma unit to clean the backside of substrates. Backside contamination of substrates can limit the quality of the front side process.

Outgassing of backside contaminants can influence the front side process, or particles on the backside can influence the image quality in a wafer stepper. The complete backside cleaning unit uses three modules to remove both organic and an-organic particles as well as organic contamination layers. This is all done in a high vacuum environment. To remove particles we will use a commercial available tacky roller. The second method to remove particles uses an UV lamp that will charge the particles on the substrate and a strong electric field to remove these charged particles from the substrate.

To remove organic contamination, for example resist residues after processing, we will use a RF plasma. The design of the RF plasma unit makes continuous cleaning over a large surface area possible. The gas in the plasma unit itself will have a pressure of 0.5 to 1 mbar. The vacuum chamber in which the complete backside cleaning unit is placed will have a pressure of around 10^{-3} mbar when the plasma unit is in use. This difference in pressure is achieved by placing the inlet of the gas in the RF plasma unit and making the outlet to the vacuum chamber very small. This design leads to a large expansion of the gas at the outlet of the RF plasma unit. The benefits of this design are that the pressure within the RF plasma unit is high enough for creating plasma and the pressure within the vacuum chamber is low enough to prevent that the whole vacuum chamber is filled with plasma.

This project focuses on backside cleaning of wafers within the "European Equipment & Materials Initiative for 450 mm" (EEMI450) under the ENIAC research program.

Within this European project, TNO is responsible for addressing contamination control issues. The concept of this backside cleaning unit can also be used to clean substrates used in roll to roll lines for solar cells or other processes that need continuous cleaning at high speed.

Plasma Science and Technology Division
Room: 201 - Session PS-ThA

Plasma Diagnostics, Sensors and Control II
Moderator: J.-P. Booth, CNRS/Ecole Polytechnique, France

2:00pm **PS-ThA1 Characterization of Atomic Oxygen Emission by PROES and Ion-Flux Measurement in an ECR Plasma Etcher**, *V. Milosavljevic*, Dublin City University, Ireland and University of Belgrade, Serbia, *B. Dolinaj, D. Gahan*, Impedans Ltd., Ireland, *N. Macgarailt*, Dublin City University, Ireland, *MB. Hopkins*, Impedans Ltd., Ireland, *S. Daniels*, Dublin City University, Ireland
For many years, optical emission spectroscopy (OES) has been successfully used for the measurement and control of plasma products in industrial plasma reactors. We have extended this technique using phase resolved optical emission spectroscopy (PROES), in a industrial electron cyclotron resonance (ECR) plasma etcher.

Experiments were conducted in a pure argon discharge with a SiO2 wafer on the biased electrode. Argon ion bombardment of the wafer liberates oxygen atoms to the discharge. Therefore, oxygen is only present at the beginning of a discharge in solid state, i.e. in the SiO2 lattice. The ECR etcher used in this experimental study has a 2.45 GHz microwave generator with a maximum power of 2kW, variable magnetic field of up 90 mT and 2MHz RF bias with maximum power of 250 W. The SiO2 wafer is mechanically clamped to the chuck to which the RF bias is applied.

In order to study the behavior of oxygen in the sheath region above the wafer an iCCD camera and high resolution spectrograph are employed and the iCCD camera is gated with respect to the 2MHz RF bias frequency. The production of oxygen is mostly due to RF voltage oscillation across the wafer induced by argon ion bombardment of its surface. The atomic oxygen spectral line intensity, from the 777 triplet, is monitored with respect to phase of the RF bias. Ion energy distribution functions, at the wafer surface, are measured using a floating retarding field energy analyzer (RFEA). The floating RFEA is is placed on the rf biased wafer surface and signal cabling is taken out through the reactor vacuum pump tunnel. This prevents the need for any modification to the reactor configuration. The RFEA sensor is 7 cm in diameter and the wafer on which it sits is 200 mm in diameter resulting in significant exposure of the wafer to ion bombardment. Phase resolved measurements are made using the iCCD camera which is operated with a repetition rate of 2 MHz synchronously (triggered) with the RF bias. The integration gate of 3.90625 ns is locked to a fixed phase position within the RF cycle (500 ns). This gives exactly 128 intervals over the 2Pi RF cycle. A variable delay between the fixed phase and the gate allows one to cover the complete RF cycle. We record strong correlation between the ion-flux and the PROES data.

2:20pm **PS-ThA2 Optical Diagnostics of Electron Energy Distributions in Low Temperature Plasmas**, *J. Boffard*, L.E. Aneskavich, R.O. Jung, C.C. Lin, A.E. Wendt, University of Wisconsin-Madison
Passive, non-invasive optical emission measurements provide a means of probing important plasma parameters without introducing contaminants into plasma systems.* Due to the dominant role of electron-impact collisions in gas-phase reactions, our investigation focuses on characterization of the electron energy distribution function (EEDF). In particular, we highlight the ability to observe EEDFs under non-equilibrium conditions in which the EEDF deviates from the Maxwell-Boltzmann form. The energy dependence of the EEDF, which varies with plasma generation method and operating conditions, has significant implications for gas phase reaction rates and is thus critical to the predictive control of plasma process outcomes. EEDFs are determined using measurements of argon emission intensities in the 650-1150 nm wavelength range and measured metastable and resonance level concentrations, in conjunction with a radiation model that includes contributions from often neglected but critical processes such as radiation trapping and electron-impact excitation from metastable and resonance levels. Results using argon emission spectra will be presented for an inductively-coupled plasma (ICP) over a wide range of operating conditions (pressure, RF power, Ar/Ne/N$_2$ gas mixtures), which show a depletion of the EEDF relative to the Maxwell-Boltzmann form at higher electron energies, in good agreement with measurements made with Langmuir probes and predictions of a global discharge model. These results are consistent with predictions of electron kinetics and can be explained in terms of reduced life times for energetic electrons due to wall losses and inelastic collisions. For Ne/Ar plasmas, analysis of neon emission spectra in addition to the argon analysis provides enhanced sensitivity to the presence of high-energy electrons. This highlights the potential utility of this method as a tool for probing kinetics of many types of low-temperature plasma systems, which are typically characterized by non-Maxwellian EEDFs.

Plasma Sources Sci. Technol. **19**, 065001 (2010).

2:40pm **PS-ThA3 Two Dimensional Laser-Collision Induced Fluorescence Measurements in Low Pressure Plasmas**, *E.V. Barnat*, Sandia National Laboratories **INVITED**
Laser-collision induced fluorescence (LCIF) is utilized to produce two-dimensional maps of electron densities and electron temperatures in helium plasmas. In this presentation, the basics of the technique are discussed and means of implementing the technique are described. To correlate the measured intensities of light emitted from the various probed states to electron densities and temperatures, a collisional-radiative model (CRM) is employed. Comparison of predictions made by this CRM to measured LCIF emanating from well characterized plasma constitutes as the calibration process of the LCIF technique. After describing the development and implementation of the LCIF technique, application of the technique to temporally and structurally interesting plasmas are discussed. Examples include ion sheaths, electron sheaths that form around biased electrodes immersed in a plasma. Also discussed are striated structures formed in a pulsed positive column. Transient evolution of these systems is discussed and future extensions of the LCIF technique are considered. "This work was supported by the Department of Energy Office of Fusion Energy Science Contract DE-SC0001939".

3:40pm **PS-ThA6 Controlled Electron Beam Excitation Method to Study Process Chemistries**, *P.L.S. Thamban*, G. Padron-Wells, University of Texas at Dallas, *J. Hosch*, Verity Instruments Incorporated, *M.J. Goeckner*, University of Texas at Dallas
We describe a method to conduct optical emission spectroscopy (OES) measurements, electron beam excitation, that can be adopted to study and quantify process chemistry species. Our method and experiment, designed to be incorporated as a diagnostic system in process tools, relies on extracting electron beam from an inductively coupled plasma. First we will present and discuss results that show electron energy dependent cross section measurements in gas mixtures specifically Fluorocarbon process chemistries. Energy dependent optical excitation cross sections of Fluorine, Oxygen and ionic species as measured with this method will be presented. The controllable excitation method and its applications to quantitative measurements of species in process chamber/exhaust will then be presented. Comparative measurements of species densities as measured with Fourier Transform Infrared Spectroscopy (FTIR) and e-beam excitation will be

4:00pm PS-ThA7 Experimental Implementation of Robust Multivariable Real-time Feedback Control Design for RIE Plasma Processing System, *Y. Zhang*, *B.J. Keville, A. Holohan, S. Daniels*, NCPST Dublin City University, Ireland

A robust multivariable real-time feedback control strategy for improving output characteristics of a reactive ion etching (RIE) plasma system is presented. Semiconductor fabrication is one of the major applications of low-pressure plasmas. During the course of manufacturing of semiconductor devices, it is often necessary to etch dielectric and/or metal layers to provide features in the layers for subsequent semiconductor processing steps. Reducing process variation is becoming ever more critical and challenging due to shrinking IC device feature dimensions and an increase in wafer size. Developments in process control are struggling to keep pace with these more stringent demands due to the fact that most semiconductor manufacturing tools are run in open loop mode. In this case, key plasma parameters such as ion flux and radical densities at the substrate surface are sensitive to drift in tool subsystems, changes in wall condition and wafer loading, for example. Disturbances to key plasma parameters may affect process metrics such as etch depth and anisotropy and result in a significant degradation in device yield and performance.

In this paper, we report the development of a robust multivariable, real-time feedback controller for the improvement of process repeatability and reproducibility of a RIE tool. Key plasma variables are sensed and their responses to the process inputs are identified experimentally. A MIMO controller then is developed and implemented to control these variables. *H-infinity* control theory and software are used for a systematic tuning procedure. This controller can effectively reduce cross-coupling effects and cope with parameter uncertainties and external disturbances in real-time in order to achieve robustness and optimal performance of the multivariable system.

4:20pm PS-ThA8 Real Time, Multivariable Control of an $SF_6/O_2/Ar$ Plasma, *B.J. Keville*, *M.M. Turner*, Dublin City University, Ireland

Plasmas of sulphur hexafluoride, SF6, mixed with oxygen and argon have been used for silicon etching in microelectronics manufacturing. Fluorine atoms produced by dissociation of SF6 etch Si with very high rates. Lateral etching, which reduces feature anisotropy, may be inhibited by the formation of a silicon oxide passivating layer on feature sidewalls. It has been demonstrated experimentally that feature profile shape is determined to a large extent by the balance between O and F radical densities at the surface of the substrate. In general, etch recipes are specified in terms of inputs such as gas flow rates, RF power and pressure and processes are run 'open loop'. 'Chamber matching', which entails ex situ statistical analysis of metrics such as etch depth, uniformity, anisotropy and selectivity, is required to ensure that each chamber produces acceptable results. However, process reproducibility may be degraded due to real-time disturbances such as MFC and match network drift, wall seasoning and substrate loading. An alternative approach which would reduce the need for chamber matching and reduce process sensitivity to disturbances would be to specify a recipe in terms of plasma parameters such as O and F radical densities, and the fluxes and energies of ions at the wafer surface and to regulate these in real time by adjusting the inputs with a suitable real time control algorithm. This presentation describes how a real time, multivariable control algorithm for an $SF_6/O_2/Ar$ plasma plasma may be designed with the aid of a control-oriented process model. The stability and efficacy of the control algorithm is demonstrated using a model of the process and a variety of simulated disturbances. Experimental implementation of the control algorithm on a laboratory capacitively coupled plasma is described.

4:40pm PS-ThA9 Maxwell Demon and its Instabilities, *CS. Yip*, *N. Hershkowitz*, University of Wisconsin-Madison

Previous experiments[1] have shown that in a low pressure, low temperature plasma, positively biasing an array of thin wires can increase electron temperature by creating an angular momentum trap to absorb cold electrons. In this experiment, such a Maxwell demon device was reproduced by welding 0.025mm tungsten wires onto stainless steel shafts, which were then covered with ceramic. This device was used to more than double the plasma electron temperatures in a multi-dipole chamber operating in the mTorr regime. Moreover, the demon is observed to reduce the cold electron population in a plasma with a bi-Maxwellian electron distribution, leaving a single Maxwellian electron distribution. However, at high positive voltage, instabilities in the kHz range prevent acquisition of meaningful temperature data. The conditions of this instability are investigated by varying neutral pressure, plasma density and applied voltage up to 150V in an argon plasma.

References

[1] K. R. MacKenzie, R.J. Taylor, D. Cohn, E. Ault, and H. Ikezi. App. Phys. Lett. Vol. 18, #12, 1971.

5:00pm PS-ThA10 Reliable Arc Detection and Arc Mitigation in RF Plasma Systems, *D. Coumou*, *R. Chouiery*, MKS, ENI Products

1. Introduction

Arc disturbances in an RF plasma source are typically short duration transients arising from discharges between the plasma and the electrode, the plasma and the chamber sidewall, or discharges within the plasma that are induced by the build-up of polymer structures. When these transients occur, a reliable means is necessary to detect the presence of the arc and to intercept the RF power delivery system to mitigate the arc event. We present a novel solution of arc detection using suitable tools from a communications equivalent paradigm that supersedes conventional heuristic methods. The proposed arc detection scheme is a quantitative approach measuring the relative arc energy of the plasma arc transient. A receiver operating characteristics (ROC) curve demonstrates the robust detection of arc transients relative to a ground truth source and yields insightful information contrasting the detection of arc disturbances in different RF sensing locations in the RF power delivery system. When an arc event is detected, arc mitigation is deployed based on suppressing the RF power with duration proportional to the detected arc energy. The rapid, and if necessary, repeated control of the RF source results in a reduction in the plasma potential to extinguish the arc source and alleviate subsequent damage. Results from PECVD and PVD tools corroborate the impact of this new scheme to significantly ameliorate thin-film manufacturing.

2. Brief Theory of Operation

A correlation function is applied to the voltage and current signals representative of the main-line electromagnetic fields sampled by an RF sensor. Analogous to a digital communication system deploying a correlation receiver, the voltage and current signals are digitally sampled, and the power between these signals is derived using well known properties of the correlation function. From the power measurement in the presence of a detected arc transient, arc energy is accumulated from fixed, non-overlapping correlation block functions. By measuring the amount of energy at the moment of detection, an RF counter mechanism is initiated by the RF power supply to reduce the plasma potential and suppress the arc source.

3. Results

Laboratory experiments are conducted and analytically summarized through an ROC curve to demonstrate the efficacy of our detection method by low false-positive occurrences. Field trials for PECVD and PVD tools outline the broad utilization of this arc detection and accompanying arc mitigation for all RF processes associated with photovoltaic device fabrication.

Advanced Surface Engineering Division
Room: 104 - Session SE+PS-ThA

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

2:00pm SE+PS-ThA1 High-Power Impulse Magnetron Sputtering of WO_3 - Influence of the Pulse Parameters on the Discharge, *A. Hemberg*, *F. Renaux, J.P. Dauchot*, Materia Nova, Belgium, *R. Snyders, S. Konstantinidis*, UMons, Belgium

Metal oxides as WO3, SnO2 and TiO2 are widely used as active layers in gas sensor applications. The sensor performances (sensitivity, selectivity, and ageing) are strongly dependent grain size, phase constitution, and material microstructure. It is accepted that in magnetron sputtering, these properties can be modified by controlling the energy and the flux of ions impinging the growing films. The ion bombardment allows modifying the nucleation process, increasing the film density, and changing texture, stress and microstructure of the coating, and ultimately improving its performances . Compared to other techniques used for thin films deposition, HiPIMS (High Power Impulse Magnetron Sputtering) enables the sputtered material to be strongly ionized. Therefore, using HiPIMS, the film properties can be altered to a larger extend as compared to conventional DC magnetron.

In this study, WO3filmshave been synthesized using reactive HiPIMS of a metallic tungsten target in Ar/O2 mixtures. A comparison is made between results obtained in HiPIMS with those obtained with a conventional DC reactive magnetron discharge (RDCMS) at identical mean power (*PD*). We discuss the influence of the pulse duration (*t*)and the target voltage (*VD*) on both the film deposition rate (*RD*)and the hysteresis behaviour. During the

HiPIMS experiments, t is varied between 10 and 50 µs and VD between 800 and 1500 V. PD is kept constant by adjusting the frequency. In reactive mode, for a given value of PD, RD increases as t and VD are increased. Comparing the HiPIMS data with those recorded during the RDCMS process, it is found that for t = 50 µs and VD = 1500 V, RD in HiPIMS is larger than for the RDCMS discharge. In order to understand this behaviour, the target current waveforms associated with these working conditions have been studied. For this particular condition (t = 50 µs, VD = 1500 V), the discharge current waveforms in metallic and reactive mode are similar. This observation wouldreveal that the target surface chemistry is identical, although the discharge is ignited either in a pure Ar or a in an Ar/O2 mixture.

The ion flux composition was also studied with a mass spectrometer located in front of the magnetron target. Time-resolved and time-averaged measurements were carried out.

2:20pm SE+PS-ThA2 A Versatile Magnetized Pulsed Cascaded Arc Source for Surface Modifications and Efficient Material Deposition, *G. De Temmerman, J.J. Zielinski*, FOM Institute for Plasma Physics Rijnhuizen, Netherlands, *L. Marot, D. Mathys*, University of Basel, Switzerland, *W. Melissen*, FOM Institute for Plasma Physics Rijnhuizen, Netherlands, *M.C.M. van de Sanden*, FOM-Instituut for Plasma Physics Rijnhuizen & Eindhoven University of Technology, Netherlands

The interaction of low-temperature plasmas with solid surfaces is at the core of numerous applications such as thin film deposition or materials processing. On the other hand, the interaction of the confined plasma with the plasma-facing materials in a nuclear fusion device can have a serious impact on the operations of a fusion device. This is especially true during plasma instabilities where surfaces are exposed to high transient heat and particle fluxes (several MJ.m-2 for 0.2-1ms). A pulsed cascaded arc source has been developed [1] to produce fusion-relevant plasmas and study the surface modifications induced by simultaneous continuous and pulsed plasma exposure.

The cascaded arc source, extensively used for thin film deposition by PECVD is used, in the Pilot-PSI linear plasma device to reproduce the plasma conditions expected in a fusion reactor with particle and heat fluxes of 1024.m-2s-1 ~10 MW.m-2 respectively. Magnetic field of up to 1.6T is used to confine the plasma. The plasma source has been modified to allow for combined pulsed/continuous operations [1]. Parallel to the DC power supply, the plasma source is connected to a capacitor bank (5kV, 8.4mF, 100kJ), which is discharged in the source to transiently increase the input power. Peak surface heat fluxes in excess of 1 GW.m-2 have been generated with pulse duration of about 1 ms (up to 1MJ.m-2). To provide more flexibility, the shape and the duration of the pulse can be adapted to the needs. The plasma conditions during the continuous and pulsed phases can be varied independently. The source can be operated in a variety of gases (Ar, H, He, N) as well as with mixed gases. Plasma properties are studied using Thomson scattering, fast visible and infrared imaging.

We will describe how synergistic effects arising from the simultaneous exposure to continuous and pulsed plasma affect the surface of a polycrystalline tungsten surface. The field of applications of the pulsed cascaded source is however not restricted to fusion-related research. Using a slightly altered configuration, the pulsed plasma source system has also opened a new route for the efficient deposition of metallic nano-particles and nano-structured thin films. Complete coverage of the surface by 10-15nm diameter nano-particles can be obtained with only a few pulses (5-10). Under different conditions, deposition rates as high as 50nm per pulse (1ms duration) have been achieved for copper and aluminium films. With a possible repetition rate of 10Hz, the system combines unprecedented deposition rates and the possibility of in-situ surface processing in between pulses.

[1] G. De Temmerman et al., Appl. Phys. Lett. 97 (2010) 081502

2:40pm SE+PS-ThA3 Pulsed Magnetron Sputtering Systems for Reactive Deposition of Oxide and Nitride Films, *J. Vlcek, J. Rezek, P. Steidl*, University of West Bohemia, Czech Republic **INVITED**
In recent years, novel high-power pulsed dc magnetron systems have been used for sputtering of films[1].

In the presentation, we report on discharge and deposition characteristics, and on film structure and properties for two different pulsed magnetron sputtering techniques.

High power impulse magnetron sputtering of zirconium target in argon-oxygen gas mixtures was investigated at a high average target power

density in a pulse, being up to 2kWcm-2. The repetition frequency was 500Hz at duty cycles ranging from 2.5 to 10%. The total pressure of the argon-oxygen gas mixture was around 2 Pa. An effective reactive gas flow control, developed by us, was used for high-rate reactive deposition of insulating, highly optically transparent ZrO_2 films. In addition to the ZrO_2 films, high power impulse magnetron sputtering was also successfully used for high-rate reactive deposition of highly optically transparent Al_2O_3 and Ta_2O_5 films. Details of the process and measured properties of the films will be presented.

Pulsed dc magnetron sputtering of B_4C-Si (25:75%) target in an argon-nitrogen (50:50%) gas mixture at the total pressure of 0.5Pa was used for deposition of Si-B-C-N films with extremely high thermal stability (even above 1500°C). The repetition frequency was 10kHz at an 85% duty cycle to avoid microarcs at the target and thus, to produce high-quality defect-free films. Prior to the deposition, target atoms were subplanted into various substrates, being at a high negative rf potential, during their etching using pulsed magnetron sputtering of the B_4C-Si target in argon gas (the same repetition frequency and the duty cycle of 20%) to enhance adhesion of the Si-B-C-N films.

[1] K. Sarakinos, J. Alami, S. Konstantinidis, Surf. Coat. Technol. 204 (2010) 1661.

3:40pm SE+PS-ThA6 Structure Evolution and Wear Mechanism in TiAlCN/VCN Nanoscale Multilayer Coatings Deposited by Reactive High Power Impulse Magnetron Sputtering Technology, *P. Hovsepian, A.P. Ehiasarian, G.K. Kamath*, Sheffield Hallam University, UK, *R. Haasch, I. Petrov*, University of Illinois at Urbana Champaign
2.5 µm thick TiAlCN/VCN coatings were deposited by reactive HIPIMS process. XTEM showed gradual evolution of the structure of the coating with thickness. The initial structure is nanoscale multilayer with sharp interlayer interfaces. This transforms to nanocomposite of TiAlCN and VCN nanocrystalline grains surrounded by C-rich tissue phase and finally changes to an amorphous carbon rich Me-C phase. In contrast deposition in similar conditions using standard magnetron sputtering produces a well defined nanoscale multilayer structure. Depth profiling by AES showed that the carbon content in the HIPIMS coating gradually increased from 25% at the coating substrate interface to 70% at the top thus supporting the TEM observations.

Energy-resolved mass spectrometry revealed that HIPIMS plasma is a factor of 10 richer in C^{1+} ions, and therefore more reactive, as compared to the plasma generated by standard magnetron discharge at the same conditions. The peculiar structure evolution in HIPIMS is discussed in relation to target poisoning effect and carbon outward diffusion during coating growth.

Highly abrasive AlSi9Cu1 alloy was dry machined using TiAlCN/VCN coated 25 mm diameter end mills to investigate the coating-work piece material interaction. Green (532 nm excitation) and UV (325 nm excitation) Raman spectroscopy was employed to identify the phase composition of the built up material on the cutting edge and swarf surfaces produced during machining. These analyses revealed formation of lubricious Magnèli phases namely V_2O_5 and graphitic carbon as well as highly abrasive SiO_2 and Al_2O_3 thus shedding light on the wear processes and coating tribological behaviour during machining.

4:00pm SE+PS-ThA7 Plasma Study and Interconnect Metallization using a Modulated Pulse Power (MPP) Hollow Cathode Magnetron, *L. Meng, H. Yu, T.S. Cho, S. Jung, D.N. Ruzic*, University of Illinois at Urbana Champaign
Modulated pulse power (MPP) magnetron sputtering, as a derivative of high power pulsed magnetron sputtering (HPPMS), was applied to a 200 mm hollow cathode magnetron (HCM) with a Cu target. The aim was to develop a more advanced ionized physical vapor deposition (IPVD) tool for applications such as interconnect metallization for sub-32 nm technologies. The MPP plasma generator, featured with 1000 V maximum pulse voltage and 550 A maximum pulse current, has a unique advantage of flexibly adjusting on- and off-time for each individual pulse, so that a long pulse packet of several milliseconds with desired waveform shapes can be generated. Distinct discharge stages were normally observed in one MPP pulse packet. Time-dependent plasma parameters were investigated using a triple Langmuir probe to help understand the MPP discharge characteristics and its performances. Plasma behaviors were shown to closely depend on the pulse waveforms and various other parameters including pulse current, repetition frequency, pressure, and distance from the target. A high electron density (n_e) of 3×10^{18} m^{-3} and an electron temperature (T_e) of 5 eV during the pulse were obtained at the substrate level, with an average power less than 8 kW. Compared with the DC magnetron sputtering at the same average power, the pulsed plasma density was an order of magnitude higher, which resulted in an enhanced ionization of the sputtered flux. As measured by an electrostatic gridded energy analyzer combined with a

quartz crystal microbalance, the Cu ionization fractions above 30% were easily achieved by the MPP sputtering on the substrate level, twice higher than those by the DC sputtering. Increasing the pulse duty ratio or reducing the pressure resulted in a stronger ionization. The performance of Cu deposition in narrow trenches (70-100 nm) using the MPP sputtering was further studied, which exhibited an improvement over the DC sputtering. Stronger pulses with higher duty ratios and a lower gas pressure were preferred to reduce the overhang and achieve better step coverage and bottom coverage.

4:20pm SE+PS-ThA8 Structural and Optical Properties of Ultra-Thin Silver Films Deposited via High Power Impulse Magnetron Sputtering (HiPIMS) on Various Adhesion Layers, *R. Jakubiak*, Air Force Research Laboratory, *L. Sun,* General Dynamics Information Technology, *N. Murphy,* Air Force Research Laboratory, *A. Waite,* Universal Technology Corporation, *J. Jones*, Air Force Research Laboratory

Multilayer metal -dielectric stacks containing noble metals such as gold, silver, and copper have myriad applications in the areas of linear and nonlinear optics and photonics. The optical dispersion of Ag makes it particularly attractive for optical interference filters and metamaterials applications. In this regard, it is essential for the Ag layers be sufficiently thin as to not inhibit transparency in the visible spectral region yet still exhibit the favorable optical dispersion of bulk Ag. This can prove difficult due to the Volmer-Weber island growth process noble metals exhibit on dielectric materials. Island formation occurs at the initial growth stages, followed by nucleation and coalescence with increasing material deposition. Below the coalescence threshold the optical dispersion does not follow that of bulk Ag and that has a detrimental effect on the optical performance of the coating. In order to lower the thickness at which coalescence occurs we've explored highly energetic deposition techniques such as high power impulse magnetron sputtering (HiPIMS) alone or in conjunction with deposition on adhesion layers of Ti, Ge or transition metal nitrides. The adhesion layers also act as barriers to oxidation of the Ag from dielectric materials incorporated in the interference coatings. Using *in-situ* spectroscopic ellipsometry the coalescence threshold of the Ag was easily monitored by noting when during the growth process the optical dispersion of the film matched that of bulk Ag. A systematic study of the how the adhesion layers and deposition parameters affected the optical properties of the Ag films was achieved by correlating structural and compositional data gather from XPS and X-ray diffraction (XRD) to the optical transmission and optical dispersion obtained by UV-Vis spectroscopy and spectroscopic ellipsometry, respectively.

4:40pm SE+PS-ThA9 Inductively Coupled Impulse Sputtering (ICIS): A Novel Technique for Ionised PVD, *A.P. Ehiasarian, D. Loch*, Sheffield Hallam University, UK

One limitation of magnetrons is their use of inhomogeneous magnetic fields which constrains deposition of magnetic materials to thin targets, complex (magnetic) alloys by erosion-dependent stoichiometry, and oxides by build-up of arc-prone insulating layers on the target edge. Inductively Coupled Impulse Sputtering (ICIS) is a new technology for physical vapour deposition based on sputtering without magnetic fields. A plasma is generated in front of the target via an inductively coupled coil driven with a 13.56 MHz radio frequency (RF) power supply. The target is then biased to a high voltage to initiate sputtering. In order to ionise significant fractions of the sputtered flux, the RF power density is pulsed with peak values in excess of 30 Wcm^{-2} to produce plasma density of the order of 10^{12} cm^{-3}. A low duty cycle of < 25% is used to achieve high peak powers and plasma densities at low average power. The degree of ionisation of ICIS of Cu and Ti in Ar atmosphere were evaluated using optical emission spectroscopy and atomic absorption spectroscopy and the film microstructure and coverage of vias was studied with cross sectional SEM. The effect of peak RF power density (P) was to increase metal ionisation degree hyperbolically. The rate of production of Ti^{1+} metal ions was proportional to ~ $P^{1.1\pm0.2}$ and was significantly faster than that of metal neutrals of ~$P^{0.66\pm0.08}$ indicating enhanced ionisation of the vapour with power. The mechanisms of ionisation will be discussed. The influence of pressure on the process was studied at a constant peak RF power density of P = 30 Wcm^{-2}. The intensity of copper and argon neutral emission rose linearly for pressures of 2.95×10^{-2} - 1.2×10^{-1} mbar and saturated at higher pressures. The deposition rate was 2 nm min^{-1} for RF-power density of 30 Wcm^{-2}, average target power of 67 W and a pressure of 1.2×10^{-1} mbar. The microstructure of Cu films was globular at 2.95×10^{-2} mbar and large-grain columnar at 1.2×10^{-1} mbar. Bottom coverage of unbiased vias with width 0.36 μm and aspect ratio of 2.5:1 increased from 15 % to 20 % as pressure increased from 2.95×10^{-2} to 1.2×10^{-1} mbar. The current work has shown that the concept of combining a high powered RF coil with a magnet-free cathode is feasible and produces very stable plasma and uniform target erosion. The experiments have shown a significant influence of power and pressure on the plasma and coating microstructure. The process is suitable for Fe, Ni and FeCo alloy deposition.

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

Plasma Science and Technology Poster Session

PS-ThP1   Anomalous Copper Contamination Observed during Hydrogen Plasma Processing, *A. Zakharov*, GlobalFoundries, Germany, *P. Geissbuhler, C. Waldfried*, Axcelis Technologies, *R. Sonnemans*, Axcelis Technologies, GmbH, Germany, *I.L. Berry III*, Axcelis Technologies

We report on an investigative study into the anomalous copper contamination observed on silicon test wafers run in hydrogen plasma processing systems using substantially oxygen-free plasmas. The copper is believed to originate from trace copper constituents of aluminum and other alloys used in construction of the vacuum system components. The transport of the copper to the wafer surface is consistent with the formation of meta-stable CuH.

Several plasma-ash systems from multiple vendors were tested using VPD/ICP-MS on silicon test wafers processed using hydrogen plus nitrogen gas mixtures. Anomalously high copper contamination levels in excess of 5×10^{11} atoms/cm^2 were measured. The copper contamination was found to increase linearly with plasma process time and the rate was highly system dependent. Clean systems tended to have higher contamination rates as compared to systems that have run large amounts of mixed processes, suggesting carbon or hydrocarbon deposits on chamber walls can somewhat suppress the CuH formation. Cycling these systems with oxygen plasmas increased the copper contamination rate. Additionally the contamination rate increased with increasing chamber wall temperature suggesting strongly that the chamber construction materials are the source of the contamination. Additionally several systems exhibited increases of cadmium, germanium and nickel. Each of these metals also has stable or meta-stable metal hydrides.

It was found that adding oxygen to the plasma in excess of 1% by volume, suppressed completely the anomalous copper contamination. VPD/ICP-MS measurement showed that 1% or higher oxygen concentration reduced copper contamination to below 1×10^9 atoms/cm2.

PS-ThP2   Real-Time Monitoring of Reactors Wall Status during Silicon and Metal Gate Etching, *A.P. Marchelli*, **G.M. Pietrogrande**, MICRON Semiconductor Italia, Italy

One major challenge in plasma etching processes for sub-65nm integrated circuits is to assure the wafer to wafer repeatability.

Particularly in plasma processes etching for IC fabrication, with metal gate, organic or metallic residues are deposited on the chamber walls. Because of the deposition of these layers a large and uncontrolled shifts in the etch process could be observed. To avoid this problem dedicated dry cleaning of the etching chamber must be developed but this methodology requires the precise knowledge of the layer coated on the reactor walls (**1**). This is not easy because of complexity of the stacks that need several steps of etching with different chemistries. Particularly the sharing of the equipments among many different process increases the complexity of layer coated. In order to assure that every wafer has been etched correctly a real-time monitoring of plasma impedance has been developed. The experiments were performed in a low pressure inductively coupled plasma reactor supplied with 13.56 MHz rf powers. Through the monitoring of dedicated equipment parameter tightly related to the plasma impedance is possible to active a dedicated fault detection control. During the wafer process, the check of this parameter along dedicated step that use only oxygen, it is possible to get the status of chamber wall in real-time; therefore is possible to activate a recovery action if necessary and don't process any other wafer. In order to validate the correlation between equipment parameter and reactors wall status etch rate test and XRF spectroscopy tests were performed. The innovation of this method consists therefore in the possibility to directly estimate the state of chamber walls during the process without having to affect measures devoted through sample (**2**).

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PS-ThP3   Reaction Process of Si Surfaces with Hydrogen Plasma, *K. Hara, M. Shinohara, Y. Takami, Y. Takaki, Y. Matsuda, H. Fujiyama*, Nagasaki University, Japan

Hydrogen plasma generates hydrogen radicals and ions in it. Both of them are important to Si technologies, such as the deposition of Si-related films, the etching of the films and so on; hydrogen radicals generate the adsorption sites by abstracting hydrogen from hydrogen terminated Si surface, while hydrogen radicals terminated dangling bonds of Si films. On the other hand, hydrogen ions also play an important role in Si etching process. Then, it is important to investigate the reaction process of hydrogen plasma with Si surfaces. We investigated the reaction processes at the different substrate bias conditions. The processes were investigated with infrared spectroscopy in multiple internal reflection geometry (MIR-IRAS). Hydrogen plasma was generated by feeding RF (13.56 MHz) power to the coil wrapped the glass tube. Hydrogen plasma was exposed to chemical oxide covered Si(100) surfaces. After the oxide layer was etched, the surface was terminated with hydrogen. Moreover, the surface was distorted, so that the atomic arrangements on the surface were changed into amorphous layer. With the increase of substrate bias which was fed with RF (800kHz) power, the formation of the amorphous layer was increased. Furthermore, we noticed that the main peak position was changed with the exposure in this process; in the initial stage, the main peak was observed between 2000 and 2030 cm^{-1}. In the middle stage the main peak was located at 2060 cm^{-1}. In the final stage the main peak was located at 2100 cm^{-1}. From the assignment of the peak positions, amorphous SiH components were formed in the initial stage; amorphous SiH$_2$ components were formed in the final stage. The peak at 2060 cm^{-1} observed in the middle stage can be assigned to the distorted SiH or hydrogen terminated vacancy. It is suggested that the kinds of hydride components are changed with the exposure.

PS-ThP4   Comparative Study on Atmospheric Pressure Plasma Modification on Packaging Material using Microwave and DBD Sources, *J.M. Hong, Y.L. Wu, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

Atmospheric plasma treatment is a very promising way to get hydrophilic or hydrophobic surface characteristics for many applications. In the food manufacturing industry there have been various kinds of technical approaches for prohibiting oxygen or water vapor penetration into products in order to preserve freshness and prolong shelf life. In this study two different types of atmospheric pressure plasmas, microwave and dielectric barrier discharge, are used on paraffin-wax coated paper. Different process recipes were applied on the packaging material and the surface modification results were evaluated. In the case of the microwave torch, a 10% improvement in hydrophobicity in terms of water contact angle measurement result and relative permeability change for water vapor was measured. The water contact angle was increased to $116\pm6°$ from $105\pm7°$ through applying a plasma treatment using a He/N2 mixture. For the permeability, three replications were prepared for each condition and weighed periodically. Each sample was prepared with a cup containing 2.0g of de-ionized water covered with treated or untreated packaging paper. According to its different treatment condition, the water loss of the plasma treated sample was 7-9% less than untreated one. This means the plasma-treated material will do better as a protective barrier against water vapor transmission. With the DBD remote plasma, a highly efficient hydrophilic process was used using nitrogen gas with small amount of air or hydrogen insertion. In order to understand the different surface reaction for the two plasma sources, the surface morphologies of treated samples were characterized by scanning electron microscopy and chemical properties were evaluated.

PS-ThP6   Inductively Coupled Plasma-Enhanced Atomic Layer Deposition of Platinum Nano-particles and Platinum Thin Films Using Ar/O$_2$ Plasma, *B.H. Liu, C.C. Kei, C.C. Yu, D.Y. Chiang, C.N. Hsiao*, National Applied Research Laboratories, Taiwan, Republic of China

Platinum nano-particles (NPs) and platinum thin films were deposited by using inductively coupled plasma atomic layer deposition (PEALD). In this PEALD process, the Ar/O$_2$ reaction plasma was applied to decompose the ligands of Pt precursor (MeCpPtMe$_3$) at varied substrate temperatures between 150 to 300 ºC. The partial pressures of Ar and O$_2$ were held at 1.5 and 0.5 Torr during the PEALD Pt NPs process. Next the PEALD Pt thin films deposited by using the lower pressure of Ar and O$_2$ at 0.3 and 0.1 Torr. X-ray diffraction (XRD) patterns show that Pt NPs and thin films are polycrystalline and a preferred orientation along the (111) plane of the fcc structure. Based on the Transmission Electron Microscopy (TEM) measurement, the growth rate of Pt NPs size and Pt thin films thickness is about 0.04 nm/cycle. The Pt thin film 4f XPS spectra consists with the Pt 4f data that observed metallic Pt peaks deposited at 200 ºC on Si wafer using Ar/O$_2$ plasma of 400 W. The step coverage was approximately 100% coated in 170 nm (open diameter) trench structures with 3.5 : 1 aspect ratio. The low resistivity of Pt NPs and Pt thin films prepared by using 600 and 200 cycles was 1.83×10^{-5} and 1.62×10^{-5} Ω-cm, respectively.

Keywords: inductively coupled plasma, PEALD, platinum NPs

PS-ThP7 Properties and Performance of TiN, TiCN Coatings on Stainless Steel for Commercial Production Equipment, *Y.L. Wu*, *J.M. Hong, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

Commercial production equipment coated with TiN and TiCN films were studied experimentally and their material properties and performance were characterized in detail. The goal is to produce a titanium nitride and titanium cabonitride coating on bare stainless steel surfaces that can resist material adhesion on the equipment surfaces. TiN and TiCN were chosen as the coating material due to their superior performance of low friction coefficient and high wear resistivity. Previous studies have shown that the friction coefficient of the coatings could be as low as 0.15 and wear rate of 6×10^{-6} mm^{3}N^{-1}m^{-1} whereas the friction coefficient was 0.6 and the wear rate was about 3 orders of magnitude higher for the bare stainless steel surfaces. In this study the TiN and TiCN coatings were made using magnetron reactive sputtering using a titanium target of 300mm in diameter and 1cm thickness with methane and nitrogen as reactive gases. The coating properties were characterized tribology testing. Adhesions of the coatings on equipment surfaces were determined with single-pass scratch tests and the friction coefficients and wear rates were found using pin-on-disc tests. Resistivity on gum base materials were also characterized with the amount of adhered gum based materials and contact angle measurements.

PS-ThP8 The Dry Etching Properties of Na$_{0.5}$K$_{0.5}$NbO$_3$ Thin Films in Inductively Coupled Plasma, *Y.H. Joo*, *J.C. Woo, C.I. Kim*, Chung-Ang University, Republic of Korea

Recently, the ferroelectric materials are possible to study many fields for the application of the ferroelectric materials. The application of ferroelectric materials in random access memory devices tends to replace both magnetic core and magnetic bubble memories. And observed high electric field tunability with low losses makes this material suitable candidate for various voltage tunable microwave devices. Ferroelectric materials usually have high dielectric constants. From several published works, it was found that the sodium-potassium niobate, Na0.5K0.5NbO3(NKN) thin films grown on oxide substrate have a great dielectric and piezoelectric characteristics. Ferroelectric NKN thin films attract attention for their superior dielectric, piezoelectric, and crystalline properties. Therefore, we can use NKN thin films for many applications including non-volatile memory, sensors, optical switches, and ultrasonic transducers. The preferential development of anisotropic etching process for NKN thin films is desirable for highly intergrated ferroelectric application. Unfortunately, a small number of papers on NKN etch behavior published. The etch characteristics are not known appropriate accurately. This fact makes some difficulties for integration of NKN in the microelectronic technology.

In this work, we investigated etch characteristics of the NKN thin films in inductively coupled plasma. Both NKN etch rate and NKN/SiO2 etch selectivity were measured as functions of gas mixing ratio, input RF power, and dc bias voltage. The chemical reaction between plasma and NKN thin film surface were investigated by x-ray photoelectron spectroscopy (XPS). Field emission Auger electron spectroscopy (FE-AES) was used for the elemental analysis of the etched surfaces. Field emission scanning electron microscopy (FE-SEM) was used to investigate the etching profile.

PS-ThP9 The Dry Etching Properties of IZO Thin Films in High Density CF$_4$/Ar Plasma, *J.C. Woo*, *C.I. Kim*, Chung-Ang University, Republic of Korea

The Indium zinc oxide (IZO) is a wide band gap transparent conducting oxide that has provoked a great deal of interest recently, due to its many potential applications. It allows the fabrication of devices with a low operating voltage, and the design of such devices will lead the way to the next generation of display technologies based on transparent and flexible devices. IZO thin films have attracted a great deal of attention because of their excellent optical transmission, high conductivity, chemical stability, thermal stability and low compressive stress. Therefore, amongst the various patterning techniques used for IZO thin films, plasma etching is preferred, because it allows for high resolution pattern transfer for optoelectronic device structures. Recently, although the growth characteristics of IZO thin films have been well optimized, the development of an efficient pattern transfer process remains to be achieved. Among the various patterning techniques, the dry etching process has several advantages over the conventional wet etching process, including high resolution and easy process automation. Moreover, there have been only a few studies relating to IZO dry etching using the high density plasma sources favored by modern microelectronic technology. As a result, the influence of the process parameters on the IZO etch rate has not been explored in detail and the IZO etch mechanism is not quite clear.

In this work, we investigated the etching characteristics of IZO thin film using a high density plasma (HDP) system. The etching characteristics of the IZO thin film were investigated in the terms of the selectivity of IZO over SiO$_2$ as a function of the etch chemistry. The chemical states on the etched surface were investigated by X-ray photoelectron spectroscopy (XPS). Field emission Auger electron spectroscopy (FE-AES) was used for the elemental analysis of the etched surfaces.

PS-ThP10 The Dry Etching Properties of TaN Thin Film Using Inductively Coupled Plasma, *J.C. Woo, Y.H. Joo, C. Li, C.I. Kim*, Chung-Ang University, Republic of Korea

PLEASE NOTE YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONE PAPER ONLY (ORAL OR POSTER) AT THE CONFERENCE. J. WOO IS CURRENTLY LISTED AS PRESENTER FOR ABSTRACT #1295Recently, to overcome these problems, conventional poly-Si gates on ultrathin SiO2 dielectric layers could be replaced by metal gates on high-*k* dielectric materials. Metal electrode/high-*k* gate stacks have already been implemented, but require continuous improvement with scaling. Currently, to integrate Hf-based high-*k* dielectric materials including HfO2, HfAlO, HfON, and HfSiO, the use of various metal gate electrode materials including TaN and TiN is being widely studied. Among these materials, TaN/HfAlO are promising candidates for replacing ploly-Si/SiO2. TaN is very attractive due to its high thermal stability, good adhesion, high melting point, and low resistivity (25 to 250 μΩ/cm). To pattern the metal electrode/high-*k* gate stack structure, etching of the metal electrode against a high-*k* dielectric layer using etching processes can be employed. In this approach, a very high etch selectivity of the metal gate electrode to the high-*k* dielectric is required because of the very thin nature of high-*k* dielectric materials. Therefore, a very high etch selectivity of the metal gate electrode to the high-*k* dielectric is also needed to minimize Si damage loss at ultrashallow source/drain regions.

In this work, the TaN thin films were etched in Cl2/BCl3/Ar and O2/Cl2/BCl3/Ar plasma. The effects of adding O2 to the Cl2/BCl3/Ar chemistry were investigated for the purpose of improving the etch selectivity of the TaN to SiO2 layer. The etching characteristics of TaN thin films were investigated in terms of etch rates and selectivity as a function of the gas mixing ratio. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) was used for elemental analysis of the etched surfaces.

PS-ThP11 Mass Spectroscopy of Metastable Atomic Species in Gas Analysis and Processing Plasmas at High Spectrometer Source Pressures, *D. Seymour, A.J. Rees, C. Greenwood, S. Davies, M. Buckley*, Hiden Analytical

The availability of particle counters which may be operated at ambient pressures of up to $2x10^{-4}$ Torr is highly desirable in many current research applications. In one field in particular, it allows mass spectroscopy of gas analysis and processing plasmas to be performed using pressures of this order in the quadrupole mass spectrometer (QMS). These pressures are much closer to those of many processing plasmas so that the sampling of neutral species, in particular, from the plasma is improved. The sampling of ion and neutral species from magnetron plasmas is a good example. The particle counter used in the present investigation, could be mounted axially so as to have a direct line-of-sight view of the sampling orifice of the QMS. Consequently, energetic neutral species such as metastable atoms of helium, which are produced in helium plasmas and have long lifetimes against spontaneous de-excitation, may travel to the detector and have sufficient energy to be counted there. The detection of metastable helium may be of importance in the study of reaction processes during hydrogen (H/HD)-deuterium (D$_2$) plasma fusion, of which the residual fusion byproduct is helium ash. Furthermore, collision processes in the ionisation source of the QMS, (including Penning ionisation), which are insignificant at the more usual source pressures of below $1x10^{-5}$ Torr, generate product ion species whose study helps the interpretation of the processes occurring in the plasma reactor. Typical data from neutral gases and plasmas in a range of gas mixtures which include helium or argon with molecular gases such as hydrogen and nitrous oxide are shown. The majority of the data presented consist of electron impact threshold ionisation efficiency curves obtained by scanning the energy of the electrons in the QMS source. The results presented are discussed in terms of processes which include collisions between metastable species such as He (2^1S and 2^3S) at 20.61eV and 19.82eV respectively[1] having radiative lifetime states of 20±2ms[2], and also other plasma constituents. The measurements suggest new avenues of research into gas analysis and processing plasmas in which energetic, long-lived, metastable species may have important roles.

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PS-ThP12 Cutoff Probe Using Fourier Analysis for Electron Density Measurement, *B.K. Na, K.H. You, D.W. Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea, *S.J. You,* Korea Research Institute of Standards and Science, Republic of Korea, *S.H. Seo, H.Y. Chang*, Korea Advanced Institute of Science and Technology, Republic of Korea

Wave-cutoff method is an electron density measurement tool. Most of the diagnostic tools, including cutoff probe, need a few seconds to measure the plasma parameters. In this presentation, a fast measurement method using Fourier analysis will be newly introduced. A wave-cutoff probe system consists of two antennas and a network analyzer. A network analyzer provides the transmission spectrum and the reflection spectrum by frequency sweeping. The plasma parameters such as electron density can be obtained through these spectra. The frequency sweeping time, the time resolution of the wave-cutoff method, is about 1~10 seconds.

We proposed a new method to use an impulse generator and an oscilloscope instead of a network analyzer. This method was named 'Fourier cutoff probe method'. A short impulse signal with a few GHz band and its transmitted signal were detected by an oscilloscope, and the Fourier analysis of the signals made a transmission spectra of plasma. The data acquisition time can be reduced with this method.

In this work, 3 diagnostic methods, Langmuir probe, network analyzer cutoff probe, and Fourier cutoff probe, were also compared. The measurement results were well matched. This method provides electron density with time resolution of 10 nano seconds, and it took about 100 milli seconds to make a measurement. This technique is found to be very useful especially in pulsed plasma. Fourier cutoff probe was 40 times faster than Langmuir probe in a pulsed plasma measurement.

PS-ThP13 Full Wave Simulation Study of Multi-mode Plasma Absorption Probes, *C.Y. Kao, W.C. Chen, K.C. Leou, C.H. Hsieh*, National Tsing Hua University, Taiwan, Republic of China

Measurement of plasma density, a key parameter that control the property of processing plasmas and hence the processing results, has been the focus of extensive studies in recent years, not only for characterization of the plasmas but also for development of tools for monitoring of the plasma based processes[1]. In this study, a multi-mode plasma absorption probe[2] was investigated by employing a full wave electromagnetic simulation using a finite element code, High Frequncy Structure Simulation (HFSS, ANSOFT CORP). The spherically-shaped probe was formed by two isolated hemispherical conductors, which was enclosed by a layer of dielectrics (alumina). In the simulation analysis, a coaxial line was attached to the spherical probe head and the "driven mode" was adoped, i.e., the wave was fed into the coaxial line and the absorption specturm, reflection coefficient vs frequency, was then analyzed. The probe was in a plasma, characterized by the collisional electromagnetic plasma permittivity, determined by plasma density, wave frequency and momentum transfer collisional frequency. Simulation results show that the absorption spectrum exhibits a number of resonances, as a result of cavity-like structure resonant modes, as well as the plasma density, similar to the results reported in a previous work based on an electrostatic analysis[2]. The electromagnetic analysis adopted in this work, however, reveals that the wave also propagates along the interface between the plasma and the coaxial cable, similar to the characteristics of a conventional plasma absorption probe[3]. This effect thus contributes to resonant peaks in the absorption spectrum that did not appear in the electrostatic analysis. A parametric study by varying the plasma density, probe size and dielectric thickness have been conducted and the results will be presented.

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PS-ThP14 Characteristics of SiO_2 Etching with $Ar/C_4F_8/CHF_3/O_2$ Gas Mixture in 60 MHz/2 MHz Dual Frequency Capacitive Coupled Plasmas, *M.H. Jeon, S.-K. Kang, J.Y. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

As the size of the semiconductor device is drastically scaled down to nano-scale, the etching technology of high aspect ratio contact (HARC) is increasingly important. To etch the nano patterned HARC, the multi-layer resist (MLR) structure conventionally composed of a PR, SiON layer, and amorphous carbon layer has been developed because it is difficult to etch HARC directly using a photoresist mask only. However, even though the etching of HARC tends to show higher etch selectivity and proper etch profile with MLR structures, for the next-generation nano-scale dynamic random access memory devices, the etching of nano-scale SiO_2 HARC using fluorocarbon plasmas is becoming more and more important.

Nanoscale SiO_2 contact holes were etched by using $C_4F_8/CHF_3/O_2/Ar$ gas mixtures in dual-frequency capacitive coupled plasmas (DF-CCPs) where 60 MHz source power is applied to the top electrode while 2 MHz bias power is applied to the bottom electrode. we added CHF_3 and O_2 gases to control the etch rate and improve the etch selectivity. Proper additive gas ratios are needed to get the high etch selectivity and maintain CD size. We measured radical intensity, etch rate and SiO_2 surface by using optical emission spectroscopy(OES), X-ray photoelectron spectroscopy(XPS), field emission scanning electron microscopy(FE-SEM) respectively.

In this study, we confirm that the etch rate and etch selectivity are varied as a function of CHF_3/O_2 gas ratios. The SiO_2 and amorphous carbon layer(ACL) etch rate are increased with increasing the HF power due to the improvement of gas dissociation. But as increasing the HF power, etch selectivity is saturated. In this study, Highest etch selectivity of about 6 is obtained at HF power 300 W, LF power 500 W, $Ar/C_4F_8/CHF_3/O_2$ = 150/20/25/5 sccm, process pressure of 20 mTorr.

PS-ThP15 An Experimental Study on Large-Area Multi-Electrode Discharge for the Deposition of Microcrystalline Silicon Thin Film for Solar Cell, *Y.S. Lee, S.H. Seo, H.Y. Chang*, Korea Advanced Institute of Science and Technology, Republic of Korea

Recently, there are many researches in order to increase the deposition rate (D/R) and improve film uniformity and quality in the deposition of microcrystalline silicon thin film. These two factors are the most important issues in the fabrication of the thin film solar cell, and for the purpose of that, several process conditions, including the large area electrode (more than 1.1 X 1.3 (m^2)), higher pressure (1 ~ 10 (Torr)), and very high frequency regime (VHF, 40 ~ 100 (MHz)), have been needed.

But, in the case of large-area capacitively coupled discharges (CCP) driven at frequencies higher than the usual RF (13.56 (MHz)) frequency, the standing wave and skin effects should be the critical problems for obtaining the good plasma uniformity, and the ion damage on the thin film layer due to the high voltage between the substrate and the bulk plasma might cause the defects which degrade the film quality.

In this study, we will propose the new concept of the large-area multi-electrode (a new multi-electrode concept for the large-area plasma source), which consists of a series of electrodes and grounds arranged by turns. The experimental results with this new electrode showed the processing performances of high D/R (1 ~ 2 (nm/sec)), controllable crystallinity (~70% and controllable), and good uniformity (less than 10%) at the conditions of the relatively high frequency of 40 MHz in the large-area electrode of 280 X 540 mm^2. And, we also observed the SEM images of the deposited thin film at the conditions of peeling, normal microcrystalline, and powder formation, and discussed the mechanisms of the crystal formation and voids generation in the film in order to try the enhancement of the film quality compared to the cases of normal VHF capacitive discharges. Also, we will discuss the relation between the processing parameters (including gap length between electrode and substrate, operating pressure) and the processing results (D/R and crystallinity) with the process condition map for μc-Si:H formation at a fixed input power and gas flow rate.

Finally, we will discuss the potential of the multi-electrode of the 3.5G-class large-area plasma processing (650 X 550 (mm^2)) to the possibility of the expansion of the new electrode concept to 8G class large-area plasma processing and the additional issues in order to improve the process efficiency.

PS-ThP16 Qualitative Research on Low-Damage Neutral Beam Etching Effect of Mechanical Properties, *Y. Nishimori, U. Shinji, K. Tomohiro,* BEANS Project, Japan, *S. Masakazu,* University of Tokyo and BEANS Project, Japan, *G. Hashiguchi*, Shizuoka University and BEANS Project, Japan

The Neutral Beam Etching (NBE) system has been expected to provide a damage-free top-down process for organic and inorganic materials and facilitate the practical development of future Nano scale devices

In order to examine the mechanical damage-free effect by NBE, we have conducted NBE surface treatment to microcantilever formed over an 8 – inch wafer from the upper surface several times, and measured the resonance frequency and the quality factor (Q-factor) of 52 cantilevers after each treatment.

The NBE treatment removes about 50nm, 100nm, and 500nm thick silicon surface layer, respectively.

The Q-factor of cantilevers is attributed by summation of various kinds of energy dissipation mechanisms such as air damping, thermo elastic damping, support, and surface dissipation.

Based on the theoretical consideration of mechanical vibration, we have designed the microcantilever having 30 um in width, 150 um in length and 2 um in thickness, by which the surface energy dissipation become dominant compared to other ones in high-vacuum condition.

In general, Q-factor is a function of the resonant frequency (fr) so that we can't argue the effect of NBE treatment from the Q-factor change as it is. Therefore we adopt the values Q-factor divided by resonant frequency (Q/fr value) which becomes independent of the thickness in case that the Q-factor is dominated by the surface dissipation and is a good parameter to represent surface dissipation.

From the viewpoint of transition of Q/fr value taken after each NBE treatment, surface dissipation of the cantilever was increased with each treatment process and saturated after adequate NBE treatment.

This indicates that surface damage introduced during fabrication process can be removed completely by slight surface etching using NBE.

In the conference, we will report the precise results of the NBE treatment experiment.

PS-ThP17 Free-standing Anodic Aluminum Oxide on Silicon Substrate by using Neutral Beam Etching, *C.K. Kim, K.S. Min, J.S. Oh, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

When the Anodic Aluminum Oxide (AAO) is used as the solid mask, compared to the patterning using electron-beam lithography and block co-polymer, the patterning using AAO is cheaper, more reliable, and easier in controlling the size and shape. However, due to the stress at the interface between the aluminum and the substrate, the alumina barrier layer is formed at the bottom of the AAO holes during the formation of AAO and it prevents direct physical and electrical contact to the substrate.

In this work, to study the effect of surface charging on the removal of the barrier layer, the Cl_2/BCl_3 neutral beam etching has been used and the results were compared with the AAO etched by an ion beam etching. By the neutral beam etching with BCl_3 containing gas mixtures, the barrier layer was successfully removed due to the formation of volatile BO_xCl_y during the etching. However, when the barrier layer was etched using the ion beam with the BCl_3 containing gas mixtures, even though AAO itself is etched, the barrier layer located near the bottom of the AAO pore was not easily etched due to the charging of the AAO pore similar to the case of conventional reactive ion etching.

PS-ThP18 Synchronous Pulsed Inductively Coupled Plasma Source for Controllable Charged Process, *K.S. Min, J.S. Oh, C.K. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

A high-density ion source derived from an inductively coupled plasma is a useful tool in the fabrication of devices. A disadvantage of the technique is that charge-induced damage can cause irreversible changes in the device properties. In order to avoid or to compensate for the non-uniform accumulation of positive and negative charges near the treated surface, a number of low-damage processes have been proposed. The most promising of these processes uses high-energy 10–1000 eV beams of fast atoms and radicals for surface treatment.

This letter reports on a different method of negative beam formation that has potential application to neutral beam etching. In particular, we obtain a flux of fast neutral atoms with narrow energy and angular distribution from an initially negative ion beam which is extracted from the discharge volume with energy of 10 – 500 eV and then neutralized. By increasing the pulse frequency of the antenna voltage to 20 kHz and applying a synchronized bipolar potential to the accelerating electrodes, it is possible to produce a high-density negative ion beam whose energy level is determined by the amplitude of the extraction potential. During the discharge, a positive potential is applied to the extraction electrode and a negative potential to the focusing electrode. In the afterglow period, these potentials are switched, allowing high-energy negative ions to escape the source. The lower and upper limits of the bipolar extraction potential on the two electrodes can be varied independently, so that the ratio of negative ions to positive ions in the resulting beam can be adjusted from 0% to 100%.

PS-ThP19 Initial Studies of a-Si Deposition and Nano-Crystallization using a Novel Reactor with Rotating Substrates, *Z. Chen, J.A. Mucha, V.M. Donnelly, D.J. Economou,* University of Houston, *Y. Lee, A.J. Akey, I.P. Herman*, Columbia University

Amorphous silicon deposition and nano-crystallization experiments were performed in a novel reactor with rotating substrates. Separate plasma sources were used for deposition (a capacitively coupled silane/helium plasma) and crystallization (an inductively coupled hydrogen plasma). Substrates were exposed sequentially and repeatedly to the deposition and crystallization plasmas for different times by varying the rotation speed. Radical concentrations in the plasma were monitored by optical emission spectroscopy while stable products were measured using a mass spectrometer. Films were characterized by spectroscopic ellipsometry (thickness, optical constants), Fourier transform infrared absorption (silicon-hydrogen bonding, hydrogen concentration), Raman spectroscopy and X-Ray diffraction (crystalline structure, degree of crystallization).

Results will be presented for different plasma operating conditions, substrate temperatures, and exposure times in the deposition and crystallization plasmas. The effect of "cross-talk" between the two plasmas and methods to prevent it will also be discussed.

Supported by the University of Houston GEAR Program and DoE

PS-ThP20 Fundamental Overview on a Controllable Optical Emission Spectroscopy Diagnostic System for Analysis of Process Chemistry, *G. Padron-Wells, P.L.S. Thamban,* The University of Texas at Dallas, *J. Hosch,* Verity Instruments Incorporated, *L.J. Overzet, M.J. Goeckner*, The University of Texas at Dallas

An Electron Beam Exciter device has been developed to perform as a controllable optical emission spectroscopy diagnostic system.1 In this design, a small to moderate amount of current extraction (0-5 mA) is necessary to achieve the desired emission signal to produce reliable optical measurements utilized in etch process monitoring and control. Current extraction from this downstream plasma system is achieved in a Non-ambipolar Flow regime.2 Non-ambipolar flow occurs when all electron thermal flux, from the exciter plasma system, exits through a uniform electron sheath formed about the perimeter of a Nozzle Aperture (area Ae) while the ions are lost to the Exciter ICP grounded wall (area Ai). Electron extraction from the exciter ICP is maximized when the ratio of the ion loss collection area (Ai) to the electron loss collection area (Ae) is proportionally equal to the square root of the ratio of the ion mass to the electron mass, and the ion sheath potential drop to the Exciter ICP grounded wall is much larger than Te/e.2,3 To investigate the degree of Non-ambipolar Electron flow in our device, we have tested a set of manufactured Nozzle extractors with different geometrical dimensions so as to discern the influence of Ai/Ae on the electron extraction process in low pressure (5-35 mTorr) Ar discharges. Strong agreement is observed between the measured plasma parameters at the ICP extraction region and the total amount of extracted current, Ie. In addition there is a measurable energy dependent response in the ratio of Ii(E)/Ie(E) indicative of electron-atom/molecule collision cross section for ionization. We have measured this ratio response in Ar and O2atmospheres. This project is funded by NSF-Grant (CBET - 0922962) and Verity Instruments.

1P. L. Stephan Thamban; J. Hosch; M. J. Goeckner. *Rev. Sci. Instrum*,2010, **81**, 013502

2B. Longmier; S. D. Baalrud; N. Hershkowitz. *Review of Scientific Instruments*, 2006, **77**, 113504 (1-8)

3S. D. Baalrud; N. Hershkowitz; B. Longmier. *Physics of Plasmas*, 2007, **14**, 042109 (1-6)

PS-ThP21   Fluid Model Simulation of Controllable E-beam, *D. Urrabazo, G. Padron-Wells, P.L.S. Thamban, M.J. Goeckner*, University of Texas at Dallas

We have developed a new chemical diagnostic based on a controlled electron beam. Specifically we make use of an inductively coupled plasma, electron extraction optics and traditional optical emission spectroscopy. In the work reported here, a computer simulation was developed which allows the use of three different models: ambipolar, classical, and revised classical. Here, we investigate both the strengths and weakness of the various models as well as determine which system characteristics can be used to enhance the system performance. These simulation results will be compared to electrical probe measurements gathered from the experimental apparatus. This work is supported in part by NSF (Grant CBET- 0922962) and Verity Instruments.

PS-ThP22   Characterization of an ECR Etching Reactor using a Retarding Field Energy Analyzer, *B. Dolinaj, D. Gahan, P. Scullin, D. O' Sullivan, MB. Hopkins,* Impedans Ltd., Ireland, *V. Milosavljevic, S. Daniels*, NCPST Dublin City University, Ireland

Microwave plasma sources are widely used in industrial plasma processing devices for their favorable characteristics. In particular, electron cyclotron resonance (ECR) reactors offer a number of desirable characteristics for plasma etching and deposition, including higher plasma density, lower ion energy, lower pressure operation, and higher uniformity compared with the conventional radio frequency (RF) type plasmas. ECR devices designed for commercial use usually provide the user with very limited access for controlling and characterizing the plasma conditions.

Retarding field energy analyzers (RFEAs) are generally used to measure the ion energy distribution function (IEDF) at electrically grounded surfaces. An RFEA can also be used to measure IEDFs at the surface of radio-frequency (RF) driven electrodes by electrically isolating it from the ground reference. The RFEA then "follows" the RF bias without disturbing it. Using the same principle, but applying grid bias signals of opposite polarity, one can also measure the electron energy distribution function (EEDF) at

the surface of RFEA. From the measured IEDFs and EEDFs it is possible to calculate the respective ion and electron flux and energy. These quantities are key parameters in plasma surface processing. Therefore, the metrological capabilities of the RFEA together with its non-perturbing in situ operation makes it a convenient diagnostic tool for characterizing plasmas in devices like ECR etching reactors.

In this work we present IEDF measurements at the surface of an RF driven electrode using a RFEA installed in an industrial ECR etching reactor. The RFEA is mounted at the RF biased electrode (on which the SiO_2 wafer is mounted) and is connected through high input impedance low pass filters to the ground referenced grid bias signals. The RFEA installation does not require any modifications to the reactor since the signal cabling is taken out to atmosphere through an existing unused port located in the vacuum pump tunnel. The discharge control parameters were varied as follows; pressure 5 to 20 mTorr, flow rate 10 to 50 sccm of pure argon and oxygen, microwave input power 750 to 1500 W, RF input power 0 to 250W, and a variety of magnetic field profiles. The radial location of RFEA has also been varied. The measured fluxes and energy distribution of the ions and electrons impacting the wafer surface are presented and discussed.

PS-ThP23 Simulations of the Radial Line Slot Antenna Plasma Source, *P. Ventzek*, Tokyo Electron America, *S. Mahadevan, L. Raja,* Esgee Technolgies, *T. Iwao,* Tokyo Electron Technology Development Institute, INC., *L. Chen, M. Funk, B. Lane, R. Sundararajan,* Tokyo Electron America, *J. Yoshikawa,* Tokyo Electron Technology Development Institute, INC., *J. Zhao,* Tokyo Electron America, *T. Nozawa, C. Tian, K. Ishibashi,* Tokyo Electron Technology Development Institute, INC.

The Radial Line Slot Antenna (RLSA) plasma source couples microwave power through a slot antenna structure and window to a plasma characterized by a generation zone adjacent to the window and a diffusion zone that contacts a substrate. The diffusion zone is characterized by a very low electron temperature. This property renders the source useful for soft etch applications and thin film processing for which low ion energy is desirable. Models of the RLSA source typically include ambipolar diffusion as an approximation enabling 2D and 3D simulations to be feasible. While such models have predictive value, they also have shortcomings when surface charging, capacitive coupling through a substrate or electronegativity are important. In this presentation we describe a self-consistent fluid model of the plasma kinetics of the RLSA source and demonstrate 3D source characteristics for benchmark argon and oxygen plasmas with and without capacitive coupling. Comparisons between the ambipolar model and self-consistent model are made.

PS-ThP24   Dual-Coil, Dual-Frequency ICP Source for Plasma Processing, *V. Nagorny, D. Lee*, Mattson Technology, Inc.

RF plasma sources used in modern plasma etch applications are required to provide a high plasma uniformity and variety of plasma controls, including independent plasma profile, plasma density and ion energy controls. They must be able to sustain a stable plasma in a very different gases and under very different conditions (gas flow, gas pressure, etc.). Finally, going forward the system has to produce a minimum impact on environment (energy consumption, EM emission). Mattson Technology has developed an etch tool with a new and efficient ICP source that uses two coils operating at significantly different frequencies (13.56 and 2 MHz) by utilizing a ferromagnetic core in a low frequency coil. Tests on the tool revealed that

· It provides high-density plasma generation, with no capacitive coupling between plasma and the source;

· There is no interference between higher and lower frequency RF subsystems;

· It provides good plasma and process profile control;

· It has wide processing window (gas pressure, gas flow, gas composition, source and bias power);

· High efficiency and stability of operation with both electropositive and electronegative gases.

PS-ThP25   Development of Inductively Coupled Hydrogen Plasma Source with a Ceramic Tube, *J. Cho, J. Yang,* PSK Inc., Republic of Korea, *S. Park, D. Lee*, Inha University, Republic of Korea

Organic photoresist in semiconductor photolithographic process has been removed by downstream oxygen plasma which is generated in a quartz chamber or tube. In case of stripping heavily ion-implanted photoresist whose surface is carbonized by energetic ions, it is sometimes necessary to add CF_4 gas to oxygen. Moreover, hydrogen based plasma begins to be used to strip photoresist coated on low-k dielectric layers, where oxygen plasma is known to degrade low-k dielectric films. However, fluorine or hydrogen ions can attack the quartz walls and generate particles. To solve this problem, plasma generation chamber should be made of materials inert to fluorine or hydrogen ions. In this work we have designed and constructed a

plasma source chamber made of ceramic tube. A 12 cm diameter ceramic tube is surrounded by a Faraday shield and wound by a 4 turn helical coil connected to 13.56 MHz RF power. There are also two turn dummy coils, which are electrically grounded, at the top and bottom sides of the 4 turn power coil. All coils have hollow square cross-section and cooling water flows through the coils. At the bottom of the 25 cm long tube an electrically grounded baffle with many small holes are located and only radicals are fed to the stripping process chamber for 300 mm wafers. Because ceramic materials usually have larger thermal expansion coefficient than quartz, larger thermal stress exists in the ceramic tube across tube thickness and at gaps between cooling coils, which results in breakage of ceramic tube. It is very important to achieve good thermal contacts between cooling water coils and tube wall and thus small temperature gradient in the tube. We have investigated the temperature profiles and thermal stress to the ceramic tube in terms of ceramic tube materials (Al_2O_3 and AlN), types of ceramic paste to glue cooling coils to the ceramic tube, size of cooling coils, thickness of ceramic tube, and RF impedance matching methods. It is found that AlN which has larger thermal conductivity than Al_2O_3 shows no breakage of tube. Size of cooling coils and types of ceramic paste have no effect on tube breakage. In case of Al_2O_3, thinner tube survives from breakage. It is confirmed that little side wall attack is observed after 1000 runs of photoresist strip by H_2/N_2 plasma.

PS-ThP26   Capability of Microwave Plasma Source for 450 mm Etching Apparatus, *S. Obama, M. Izawa, H. Tamura,* Hitachi High-Technologies Corp., Japan, *K. Maeda*, Hitachi Ltd., Japan

To produce semiconductors at low cost, the transition to 450 mm-sized wafers is being considered. For semiconductor fabrication on 450 mm substrates, the etching performance is expected to equal or exceed 300 mm substrate capability with improved productivity requirements. A 450 mm substrate capable apparatus was developed on a proven plasma source using microwave electron cyclotron resonance (ECR) currently utilized for 300 mm equipment. We have evaluated plasma uniformity by using: 1) Single Langmuir probe with -50 V bias to measure ion current flux (ICF) distribution in the plasma reactor. The plasma generated area and the spatial distribution of ICF were scanned in the radial and z-axis directions in the reactor. 2) A 41-point wafer stage to measure ICF distribution. 3) Etch rate uniformity of poly-Si and SiO2 using coupon samples attached on 450 mm bare Si wafers. We used HBr/Cl2/O2/Ar gas and 0.1-10 Pa pressure range as test conditions.

We found that the high density plasma generated at the ECR zone and the shape of the plasma was ring-shaped. This ring-shaped plasma diffused and became increasingly uniform, finally becoming almost flat at a height of 25 mm above the wafer stage. To evaluate ICF distribution of the wafer stage, 41 pads were used to measure plasma density distribution using about 500 test conditions. By controlling the magnetic fields, non-uniformity of ICF below ±5% was achieved for several test conditions of gas and pressure. Poly-Si and SiO2 etching rate were observed to be very similar to rates seen using 300 mm substrate equipment with non-uniformity below ±1% within a wafer.

In this preliminary study, though we need more process evaluation by using whole blanket wafers and patterned wafers, the microwave ECR plasma apparatus for 450 mm wafers achieved the same level of process performance as the 300 mm equipment.

PS-ThP27   Plasma-based Techniques for Doping Three-Dimensional Structures, *G. Papasouliotis, K. Han, H. Persing, L. Godet*, Varian Semiconductor Equipment Associates, Inc.

Increasingly stringent demands for maximum device speed and control of random dopant fluctuation effects dictate changes in device architecture, with FinFET adoption becoming a viable possibility for device scaling at and beyond the 15 nm technology mode. Three-dimensional architectures pose a fundamental challenge for traditional ion beam implant processes, since, depending on the aspect ratio of the structure, certain sections can be inaccessible to the dopant beam. Plasma immersion ion implantation (Plasma Doping), which has been adopted as an enabling, production-worthy technology in the ultra high dose and low voltage regime for advanced DRAM device nodes, can be an alternative capable of overcoming these limitations. In this work, experiments are carried out using a VIISta PLAD system, which uses an ICP source to generate a discharge and a series of negative dc voltage pulses applied to the substrate to accelerate ions towards it. Silicon trenches are implanted using an AsH3-containing gas mixture in the PLAD reactor. The presence and activation of the N-type dopant onto the #D structures are characterized by physical (Secondary Ion Mass Spectrometry, Transmission Electron Microscopy, Energy Dispersive X-ray spectroscopy) and electrical methods, and discussed in conjunction with analysis of the gas phase in the plasma chamber. Our experimental results indicate the occurrence of a combination of implant and ion assisted deposition processes. It is shown that balancing the constituents of a plasma doping process and plasma characteristics such

as electron temperature and gas phase composition is required to allow dopant incorporation into sidewalls of 3D structures.

PS-ThP28 Study of Low-k Dielectric Damage in a Radial Line Slot Antenna (RLSA) Reactor, *Y. Susa*, Tokyo Electron Technology Development Institute, INC., *R. Sundararajan, J. Zhao, L. Chen*, Tokyo Electron US Holdings Ltd., *T. Nozawa*, Tokyo Electron Technology Development Institute, INC., *J.A. Mucha, D.J. Economou, V.M. Donnelly*, University of Houston, *R. Wise*, IBM Research

Low-k dielectrics are widely used as insulating materials in ULSI circuits. In BEOL processes, etching of low-k layers can cause serious damage, especially during photoresist ashing. In this work, a Radial Line Slot Antenna (RLSA) microwave plasma source was used in an effort to minimize damage to low-k dielectrics as a result of photoresist ashing. The focus of the work was ashing in CO_2–containing gas mixtures of test wafers partially covered with blanket low-k and photoresist layers. Damage to the SiCOH (k=2.5) low-k dielectric was characterized using Spectroscopic Ellipsometry, FTIR and XPS. It was found that low pressure (~ 5 mTorr) and high bias voltage (~2000 V) were beneficial in terms of minimizing low-k damage. XPS revealed that, under these conditions, an oxide "crust" formed on the surface of the low-k, that apparently protected the underlying material. Low pressure favors an enhancement of the ratio of the ion –to- O-atom flux. Energetic ions can be instrumental in forming this oxide crust by near surface ion implantation. The oxide hinders diffusion of the (already low density) O atoms into the low-k film resulting in minimal damage.

PS-ThP29 New Pulsed Plasma Generator for producing near Arc Free Discharges for Reactive Magnetron Sputter Processes, *R. Chistyakov, B. Abraham*, Zond Inc/ Zpulser, *J.Y. Park*, SEMICAT Inc

New pulsed plasma generator for reactive magnetron sputter processes was developed. (old sentence)

A new pulsed plasma generator for reactive magnetron sputter processes has been developed. (new sentence)

Compare with existing pulsed DC plasma generators new generator has high current capabilities in the range of 100 – 300 A.(old sentence)

Compared to existing pulsed DC plasma generators, the new generator has high current capabilities in the range of 100 – 300 A. (new sentence)

In proposed method near arc free magnetron discharge in reactive atmosphere can be generated by adjusting the frequency and amplitude and shape of the voltage pulses. (old sentence)

In the proposed method, near arc free magnetron discharge in reactive atmosphere can be generated by adjusting the frequency and amplitude and shape of the voltage pulses.(new sentence)

The application of new pulse plasma generator for reactive sputtering of SiN, SiO_2, AlN and TiO_2 films at ENDURA 200 mm tool (AMAT) will be discussed. (old sentence)

The application of new pulse plasma generator for reactive sputtering of Si_3N_4, SiO_2, AlN and TiO_2 films at ENDURA 200 mm tool (AMAT) will be discussed.(new sentence)

Friday Morning, November 4, 2011

Spectroscopic Ellipsometry Focus Topic
Room: 209 - Session EL+AS+EM+MS+PS+TF-FrM

Spectroscopic Ellipsometry: Future Directions and New Techniques
Moderator: H. Wormeester, MESA, The Netherlands

8:20am EL+AS+EM+MS+PS+TF-FrM1 Current Trends and Future Outlook for Spectroscopic Ellipsometry, *J.N. Hilfiker*, B. Johs, C.M. Herzinger, T.E. Tiwald, J.A. Woollam Co., Inc. **INVITED**
This talk reviews the significant developments in spectroscopic ellipsometry (SE) in areas including extending spectral range, improving accuracy, and enhancing speed. Current SE applications owe much to hardware and software developments of the past. Thus, today's research efforts may reach full potential for applications years or even decades from now. With this in mind, we point to the current state-of-the-art and what this may mean for future SE applications.

Three important areas will be explored. First, there has been a continual trend to expand SE wavelength range. This has included extensions to both shorter and longer wavelengths. For the latter, there is current development into the THz. More immediate benefit may come from smaller SE extensions from the ultraviolet to the near infrared. For example, further near-infrared extensions help to characterize modern transparent conductive oxides (TCOs), used in both inorganic and organic photovoltaic stacks.

Second, we look at the search for improved SE accuracy. Substantial improvements have come with the development of new ellipsometer technologies, progressing from rotating analyzer/polarizer to rotating compensator and now dual-rotating compensator ellipsometers. In addition to improved accuracy, this technology provides advanced measurements, including the complete Mueller-matrix. This will open SE characterization to new applications of anisotropic, nanostructured, and even patterned thin films. Accuracy enhancements must be compatible with the expanding SE spectral range. Infrared SE has overcome many non-ideal optical components to provide measurements competitive to standard FTIR measurements.

Third, we look at the quest for improved measurement speed. This development is constrained by the previous requirements. The benefits of a wide spectral range generally outweigh speed requirements; otherwise laser-based ellipsometry would still have a strong foot-hold. Thus, compromises are made depending on application. Current instrumentation typically utilizes detector arrays for multi-channel SE measurements.

To conclude, we will look at the SE outlook and how it may take advantage of wavelength range, accuracy, and speed. In-line and in-situ SE measurements show special promise. Significant improvements in instrumentation, computing speed, and software are now making these applications more feasible. In addition, there are novel ideas to provide sample access and overcome non-ideal measurement conditions for in-line and in-situ SE. Significant progress in many different areas promises to extend ellipsometry into new areas – many of which are being studied by researchers today.

9:00am EL+AS+EM+MS+PS+TF-FrM3 THz Optical Hall-effect and MIR-VUV Ellipsometry Characterization of 2DEG Properties in a HfO$_2$ Passivated AlGaN/GaN HEMT Structure, *S. Schöche*, U. of Nebraska - Lincoln, *J. Shi*, Cornell U., *A. Boosalis, P. Kühne*, U. of Nebraska - Lincoln, *C.M. Herzinger, J.A. Woollam*, J.A. Woollam Co., Inc., *W.J. Schaff, L.F. Eastman*, Cornell U., *V. Darakchieva*, Linkoping U., Sweden, *M. Schubert, T. Hofmann*, U. of Nebraska - Lincoln
Nitride based high electron mobility transistors (HEMT) utilize the formation of a two-dimensional electron gas (2DEG) at the interface between GaN and AlGaN due to a difference in spontaneous polarization. It is known that surface traps significantly influence the electrical properties of this 2DEG. Accurate knowledge about the influence of surface passivation on the channel properties is crucial. The device performance is governed by the mobility, the sheet charge density, and the effective mass of electrons in the 2DEG. These parameters are typically determined by electrical Hall effect (EHE), Shubnikov-de Haas (SdH), or cyclotron resonance (CR) measurements. Commonly these experiments require very low temperatures and high magnetic fields. Complex contact configurations are required for SdH and EHE and the ability to locate the 2DEG and possible parallel current paths is limited.

We present non-contact, optical measurements of free-charge carrier mobility, sheet density, and effective mass parameters of the 2DEG for a HfO$_2$-passivated AlGaN/GaN HEMT structure at room temperature.

Spectroscopic ellipsometry in the spectral range from THz and Mid-IR to VUV and THz optical Hall-effect (generalized ellipsometry in magnetic field) (OHE) are employed.

The MIR measurements are performed for analysis of the heterostructure constituents' layer thickness, phonon modes, and volume free charge carriers. The phonon mode parameters were found to be in excellent agreement with literature values and the existence of significant volume charge carrier concentrations could be excluded. NIR to VUV ellipsometry is used to determine the thickness of the thin top layers. From a line-shape analysis in the VUV spectral range the optical constants of the HfO$_2$ passivation layer could be extracted. An amorphous structure of the HfO2 passivation layer could be confirmed by comparison with existing studies in literature.

OHE in the THz spectral range is performed for characterization of the 2DEG channel parameters. A classical Drude model for free charge carrier contribution to the dielectric function was applied to determine the sheet density, the carrier mobility, and the effective mass of the 2DEG electrons. The electron effective mass of (0.22±0.04) m$_0$ extracted here using OHE corroborates the values found in previous SdH and CR studies. The values for the high-frequency sheet density and carrier mobility obtained by the optical investigations in the THz spectral range are in excellent agreement with results from dc EHE measurements indicative within linear Boltzmann transport theory for frequency-independent carrier scattering mechanisms of the 2D carrier distribution.

9:20am EL+AS+EM+MS+PS+TF-FrM4 Vector-Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films, *D. Schmidt, C. Briley, E. Schubert, M. Schubert*, University of Nebraska - Lincoln
Sculptured thin films are self-organized and self-assembled three-dimensional nanostructures with tunable geometries. These artificial nanostructured thin films exhibit highly anisotropic physical properties, which mainly depend on their specific geometry.

Slanted, highly-spatially coherent, columnar nanostructure samples were prepared by glancing angle electron-beam deposition. Glancing angle deposition is a bottom-up fabrication technique that employs a physical vapor deposition process at oblique angles where the trajectory of the incoming particle flux is not parallel to the substrate normal. The technique allows to engineer the columnar film structure and is today amongst the most promising self-organized fabrication processes in micro- and nanotechnology.

We present and discuss the novel approach of vector-magneto-optical generalized ellipsometry on ferromagnetic permalloy nanostructured thin films carried out at room temperature. Investigations have shown that the metal alloy thin films are highly transparent, reveal strong form-induced birefringence, and exhibit intriguing magneto-optical anisotropy. Spatial magnetization orientation hysteresis and magnetization magnitude hysteresis properties are studied using a three-dimensional Helmholtz coil arrangement. This particular octupole setup allows for arbitrary magnetic field directions at the sample position with field strengths up to 200 mT while optical access is granted for reflection and transmission-type ellipsometry measurements. Analysis of data obtained within this unique vector-magneto-optic setup reveals magnetization anisotropy of the permalloy slanted nanocolumns and gives insight into switching behavior of confined magnetic domains.

9:40am EL+AS+EM+MS+PS+TF-FrM5 THz Dielectric Anisotropy of Metal Slanted Columnar Thin Films, *T. Hofmann*, D. Schmidt, A. Boosalis, P. Kühne, R. Skomski, University of Nebraska-Lincoln, C.M. Herzinger, J.A. Woollam, J.A. Woollam Co., Inc., M. Schubert, E. Schubert, University of Nebraska-Lincoln
Sculptured thin films (STFs) present an interesting class of self-organized, artificially made materials with three-dimensional, highly spatially coherent arrangements of nanostructures. Contemporary interest in materials for terahertz (THz) electronic, optoelectronic, and optical applications is redrawing attention to STFs that may enable designed optical properties for the THz frequency region.

We report on the anisotropic optical dielectric functions of a metal (cobalt) slanted columnar thin film deposited by electron-beam glancing angle deposition for the THz frequency domain using generalized spectroscopic ellipsometry. A simple anisotropic Bruggeman effective medium dielectric function homogenization approach is successfully employed to describe the observed optical response. This approach describes isolated, electrically conductive columns which render the thin film biaxial (orthorhombic). The anisotropy induced by the columnar film structure is very large. The anisotropic Bruggeman effective medium approach predicts upon slight modifications of Drude, fraction and/or depolarization parameters that

targeted optical properties of STF in the THz range can be achieved by variation of slanting angle, lateral column density, and material.

10:00am EL+AS+EM+MS+PS+TF-FrM6 A Compact High-speed Spectroscopic Ellipsometer, *G. Chin*, ULVAC Inc., Japan
Recently, we developed a compact, high-speed spectroscopic ellipsometer. It analyzes the spectrums obtained from the polarization interference occurring between two multiple-order retarders which snapshot the wavelength distribution of the sample's spectroscopic polarization parameters. This innovative spectroscopic ellipsometer can measure the thickness and optical constants of thin films at a dramatically fast speed. Its acquisition time is as short as 10 ms. It does not require the conventional complex mechanical or active components for polarization-control, such as a rotating compensator and an electro-optical modulator. It can open great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. For example, it was integrated into the deposition tool and successfully measured thin films in the vacuum chamber.

This paper describes the principle, system configuration and our innovative efforts on developing the compact high-speed spectroscopic ellipsometer. Some typical application data will be also introduced, such as in line and in situ measurements for photovoltaic, flat panel display and semiconductor industries.

10:20am EL+AS+EM+MS+PS+TF-FrM7 Ellipsometry Porosimetry (EP): In Situ Spectroscopic Ellipsometry Measurements Coupled with Pressure Controlled Adsorption of Organic Vapors to Study Properties of Nano-Porous Thin Films, *J.P. Piel, L. Kitzinger, A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France
Ellipsometric porosimetry (EP) is a non contact, non destructive technique that is cited as a reference technique for porous thin film analysis [1, 2]. As it is based on a spectroscopic ellipsometric measurement, the technique allows the precise determination of the refractive indices and thickness of the porous films. The advantage of these EP tools is that the combination of this well established spectroscopic ellipsometric (SE) technique with a suitably adapted adsorption chamber permits access to all the information obtained by classic adsorption experiments (e.g. BET) on thin films with an excellent sensitivity. Information such as open and closed porosity, pore size distribution etc... can be thus obtained.

In addition the EP allows access to a multitude of information that the classic equipment does not. For example, Spectroscopic Ellipsometry allows to follow the variation of the sample thickness during the adsorption experiment, leading to the determination of the Young's Modulus for the thin films. This will be presented. The technique is highly sensitive to the detection of interfaces; it is thus possible to detect a porosity gradient or to study a multilayer structure and thereafter simultaneously plot the two corresponding adsorption isotherms [3]. In the same manner, the instrument permits the use of a range of different gases adsorptive in order to tailor the probe molecule to the morphology and to the chemistry of the porous layer at ambient temperature [4]. We thus obtain information on the chemistry of the pores within the layer, before, during and after the adsorption experiment. Recent developments include the implementation of the FTIR interferometer SE extension to the EP system. It allows a precise characterization of the chemistry of the pores within the layer. We thus obtain information on the chemical bonds present in the layers before, during and after the adsorption experiment. Preliminary results will be presented.

Specifically, this fundamental technique permits the thorough characterization of porous thin film samples. We will demonstrate some of the different features of the EP technique with regards to the morphological and chemical properties of the porous thin films. Additionally, we will illustrate the technique for various thin film applications such as solgel thin films, nanofilms for catalysis, photovoltaic cells, fuel cells, optical sensors, and bio-compatible materials to name but a few.

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[3] A. Bourgeois et al, *Thin Solid Films* **455-456**, 366 (2004).

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Plasma Science and Technology Division
Room: 201 - Session PS-FrM

Plasma Modeling
Moderator: K. Bera, Applied Materials, Inc.

8:20am PS-FrM1 Delivering Activation Energy to Surfaces in Atmospheric Pressure Plasmas: Local and Remote, *Z. Xiong, N.Yu. Babaeva, M.J. Kushner*, University of Michigan
Non-equilibrium atmospheric pressure plasmas (APPs) are efficient at producing chemically reactive environments by electron impact dissociation and ionization of feedstock gases. Other than generating UV photon fluxes, APPs are not thought to be sources of non-thermal activation energy in the form of energetic ions or hot atoms. Athough mean free paths of ions may be less than 1 micron, the transient production of electric fields of 100s kV/cm to 1 MV/cm when the ionization fronts of streamers intersect with surfaces provide the possibility of accelerating ions to many to tens of eV. This high quality delivery of activation energy is a function of not only the properties of the streamer but also depends on the properties of the surface. For example, delivery of high energy ions to the surface of a bulk polymer may differ from a layered polymer due to differences in their capacitive properties. These differences extend to organic material as well – the deliver of energetic ions to cells and tissue will depend on their respective dielectric properties and those of the surrounding medium. Delivery of high quality activation energy in any form (photons or ions) to remote sites or locations is challenged by line-of-site issues and the charging of surrounding materials that may reduce ion energies. Being able to deliver activation energy to the crevices of rough surfaces may be important in the context of plasma sterilization. In this talk, results from modeling studies of atmospheric pressure plasma streamers and jets intersecting with dielectric surfaces will be discussed. The delivery of activation energy by ions and photons to rough surfaces will be discussed in the context of polymer modification and sterilization. Plasma sources will include directly applied dielectric barrier discharges and remote plasma source delivered by capillary tubes. * Work supported by the Department of Energy Office of Fusion Energy Sciences.

8:40am PS-FrM2 Kinetic Effects in Low Pressure Capacitively Coupled Plasmas, *A. Likhanskii, P. Stoltz*, Tech-X Corp.
We present results of particle-in-cell/Monte Carlo collision simulations of kinetic effects in low pressure capacitively coupled plasma discharge.[1] In particular, we examine discharges of various gases (including Ar , Xe, and others) in the pressure range of 10s of mT and the frequency range of 10s of MHz. We track the formation of high energy electrons (*e.g.,* at the ionization threshold or greater) as a marker for enhanced ionization, and look at the effects of elastic and inelastic collisions on the formation of these high energy electron bunches. [2,3] We show results for 2D and 3D simulations where we include density gradient effects, and results for plasma chemistry effects on the bulk electron energy distribution function and the ion energy distribution function at a plasma surface interface. We discuss the role of the bunches on electron heating in the plasma bulk and on their presence on how electron heating is treated in fluid simulations of plasma sources.

9:00am PS-FrM3 Challenges in Modeling of Plasma Interactions in Medicine and Biology: What Insights Can You Expect?, *N.Yu. Babaeva, M.J. Kushner*, University of Michigan **INVITED**
The development of technologies for the plasma treatment of living tissue is in large part based on controlling plasma sources to deliver the desired fluxes of radicals and ions to surfaces. This process is complicated by scientific and technical issues. From a scientific standpoint, although it is generally accepted that reactive oxygen species (ROS) and reactive nitrogen species (RNS) are important in, for example, wound healing, sterilization and cancer treatment, it is not clear which species and in what proportions are optimum for each type of treatment. The situation becomes more complex when considering the UV photons, energetic ions and electric fields produced by the discharge which also interact with the tissue. From a technical view point, the interaction between the tissue (and wounds in particular), the surrounding materials and the plasma can significantly affect the plasma. For example, the shape of the wound and the permittivity of the fluid in a wet wound can warp local electrical fields which then feed back to the plasma. Given this complexity and interdependencies, computer modeling of plasma-tissue interactions might provide insights to these interactions. In this talk, results from computer modeling of plasma-tissue interactions will be discussed. The modeling platform solves for charged particles, neutral and photon fluxes while also solving Poisson's equation, and resolving spatial scales on reactor-to-cellular levels. Plasma transport through gases and liquids are included. Two types of plasma sources will be

considered - dielectric barrier discharges (DBDs) where the plasma is in direct contact with the tissue and remote plasma jets, where dominantly neutral species and photons reach the tissue. We will discuss the treatment of wounds through a liquid layer covering exposed cells wherein the blood serum contains blood platelets. The characteristics of the plasma sources, and the interaction of plasma generated species and electric fields with the wound, fluid and underlying cells will be discussed.

10:00am PS-FrM6 Magnetic Field - Plasma Interaction in Low Pressure VHF Capacitively Coupled Plasmas using PIC-MCC/Fluid Hybrid Model, *K. Bera*, *A. Agarwal, S. Rauf, K. Collins*, Applied Materials, Inc.

Low pressure magnetized capacitively coupled plasmas are extensively used for advanced microelectronics device fabrication. Due to the long mean free path of electrons in this regime, kinetic effects characterize the plasma dynamics in low pressure discharges. To take into account the kinetic effects, a hybrid 2-dimensional (2D) plasma modeling software has been developed that couples a particle-in-cell (PIC) model for charged species with a fluid method for neutral species. The electron motion due to electric and magnetic fields is incorporated in 3-dimensional velocity space using the Lorentz force law. The PIC model uses the Monte Carlo Collision (MCC) method to account for collision processes. The fluid model for neutral species takes into account species transport in the plasma, chemical reactions, and surface processes. Capacitively coupled rf plasmas in Ar have been computationally investigated for a 2D parallel plate plasma reactor in Cartesian co-ordinates. The inter-electrode gap is 5 cm (in y-direction). The bottom electrode is powered using a 60 MHz very high frequency (VHF) source, and the top electrode is grounded. The two electrodes are separated by quartz inserts. Ar plasma is simulated for a range of magnetic fields (25 - 100 Gauss), pressures (10 - 50 mTorr) and rf voltages (100 - 300 Volts). In this range of magnetic fields, the electrons are magnetized due to a small Larmor radius while the ions remain non-magnetized. For a symmetric reactor configuration without magnetic field, the plasma is symmetric, and the peak in plasma density occurs at the center plane between the top and bottom electrodes. The electron density increases with increase in pressure and rf voltage. With magnetic field in the x-direction (parallel to the electrodes), the plasma becomes more confined. When the magnetic field is applied in the z-direction, orthogonal to the electric field, the E x B drift is observed, and the plasma becomes asymmetric. When the magnetic field direction is reversed, E x B drift reverses, therefore, the direction of plasma asymmetry reverses. The effect of magnetic field on plasma symmetry will be examined. In addition, results from the kinetic simulation will be compared to corresponding results from a fluid plasma model.

10:20am PS-FrM7 Simulations of SF$_6$ Plasma Etching in the GEC Reference Cell, *S. Lopez-Lopez,* Quantemol - University College London, UK, *J.J. Munro, D. Brown,* Quantemol Ltd., UK, *J. Tennyson*, University College London, UK

Electrically driven plasmas containing halogens are very used in different material modification and surface cleaning processes. Sulfur Hexafluoride (SF$_6$) is used industry-wide in a range of processes for the dry etching of silicon or silicon dioxide for microelectronic feature definition, such as the Bosch process. However, the performance and efficiency of different processes and machines can vary widely, and the use of simulations can give us significant insight into the optimization problem and provide a low cost means for further development. That is especially relevant in the case of SF$_6$, given its environmental impact, with a Greenhouse Warming Potential that is 22,000 times that of CO$_2$. It is therefore vital to use SF$_6$ sparingly and efficiently in every process, and simulation can help to find ways of remediating harmful waste gases and optimize the process for typical processing goals (e.g. etch rate, uniformity) as well as improving SF$_6$ consumption efficiency and other environmental measures.

A key aspect of the plasma processes here considered is that some type of work is done at the plasma / surface boundary layer, and realistic simulations must therefore incorporate the surface material and the etch product chemistry. This increases drastically the complexity of the problem but is the only way to represent all of the appropriate physics. Radical species from the surface entering the gas phase will take part in the phase and surface reactions that are associated with the parent gas, including negative ion formation and electron dissociation among others.

Here we present 2D simulations of an inductively driven SF$_6$ silicon etch process in the GEC Reference Cell [1], building upon previous calculations of SF6 plasma chemistries using Quantemol-P [2]. Etch rate, pressure and power trends along with chamber wide contour plots of gas-phase species concentrations and fundamental plasma properties are considered. We have found a good agreement with experimental results [3], which validates the underlying model and points to the important role of simulation-assisted plasma process development and optimization.

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10:40am PS-FrM8 Simulation of InP Etching under ICP Ar/Cl$_2$/N$_2$ Plasma Discharge: Role of N$_2$ in the Sidewall Passivation, *R. Chanson, A. Rhallabi, M.C. Fernandez, Ch. Cardinaud, J.P. Landesman,* Institut des Matériaux Jean Rouxel (IMN), France, *S. Bouchoule, A. Talneau,* Laboratoire de Photonique et de Nanostructures (LPN), France

InP-based optoelectronic devices need reliable dry etching processes characterized by high etch rate, profile control and low damages. High density plasma etching, using inductively coupled plasma ICP reactors, has been found to be very important for the transfer of patterns from the mask to InP substrate and InP-based layers. In order to investigate the role of N$_2$ in the InP etching process under Cl$_2$/Ar/N$_2$ plasma discharge, we have developed an InP etching simulator permitting to determine the InP etch profile evolution through the mask as a function of the operating conditions and the initial mask geometry.

The InP etching simulator is divided in three modules: the global kinetic model of Cl$_2$/Ar/N$_2$ ICP plasma discharge is based on 0D approach which allows to calculate the averaged densities of neutrals and ions as well as the electron density and electron temperature versus the machine parameters. The resolution of the differential equations associated to the mass balance of each considered specie coupled to charge neutrality equation and the differential power balance equation from t=0 until the steady state allows to determine all reactive specie densities as well as their fluxes into the InP substrate. n$_e$ and T$_e$ calculated from the plasma global kinetic model are introduced in the sheath model to estimate the average sheath thickness. The Monte-Carlo technique is used to study the ion transport in the sheath. The calculation of energies and angles of all positive ions impinged on the substrate allows determining the angular and energy distribution functions of positives ions. Such distribution functions with Cl, N and positives ions fluxes are introduced as input parameters into the etching model. The later is based on the cellular approach combined to the Monte-Carlo method which the considered domain (InP substrate and mask) is discretized on 2D uniform cells which each cell represents a real number of In sites. The fluxes of neutral species and positive ions are introduced as input parameters into the etching model. All the particle surface interaction processes like adsorption of atomic neutrals Cl and N on InCl$_x$N$_y$ surface sites, desorption of InCl$_x$ sites, sputtering of both InCl$_x$N$_y$ and mask by positive ions and redeposition of InCl$_x$ sites are described in probabilistic ways. Simulation results show the effect of the N$_2$ on the passivation of the lateral surfaces and as consequence the improvement of the etch profile anisotropy. However, a diminution of the etch rate by increasing the percentage of N$_2$ is observed. The simulated etch profiles are compared to those obtained by the experiments and the good agreements are obtained.

11:00am PS-FrM9 Three-Dimensional Modeling and Formation Mechanisms of Atomic-Scale Surface Roughness during Si Etching in Chlorine-Based Plasmas, *H. Tsuda, Y. Takao, K. Eriguchi, K. Ono*, Kyoto University, Japan

Three-dimensional measurement and prediction of atomic-scale surface roughness on etched features become increasingly important for the fabrication of next-generation devices; however, the feature profiles are too small or too complex to measure the surface roughness on bottom surfaces and sidewalls of the etched features. To predict the surface roughness on atomic or nanometer-scale, we have developed our own three-dimensional atomic-scale cellular model (ASCeM-3D) [1] and feature profile simulation. Emphasis is placed on a better understanding of the formation mechanisms of atomic-scale surface roughness during Si etching in chlorine-based plasmas and the relationship between the ion incident energy and angle and etched feature profiles.

In the ASCeM-3D model, the simulation domain is divided into a number of small cubic cells of $L = r_{Si}^{-1/3} = 2.7$ Å, where $r_{Si} = 5.0 \times 10^{22}$ cm^{-3} is the atomic density of Si substrates. Ions and neutrals are injected from the top of the simulation domain, and etch and/or sputter products are taken to be desorbed from etching surfaces into microstructural features, where two-body elastic collision processes between incident ions and substrate atoms are also taken into account to analyze ion reflection on etched feature surfaces and penetration into substrates. The ASCeM-3D takes into account surface chemistries based on the Monte Carlo (MC) algorithm [2-4], including adsorption and reemission of neutrals, chemical etching, ion-

enhanced etching, physical sputtering, and redeposition of etch and/or sputter products on feature surfaces.

Numerical results indicated that nanoscale convex features increase in size with increasing etching or plasma exposure time, and surface roughness increases with increasing ion incident energy. The ripple structures of etched surfaces were found to occur depending on incident angle of ions. Ion reflection or scattering on etched surfaces strongly affects the evolution of feature profiles and surface roughness on atomic scale.

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11:20am **PS-FrM10 Control of the Ion Energy Distribution on a Plasma Electrode**, *P. Diomede, D.J. Economou, V.M. Donnelly*, University of Houston

The energy of ions bombarding the substrate is critical in plasma etching and deposition of thin films, especially when precise etching without damage is required. The ion energy distribution (IED) may be controlled by applying "tailored" bias voltages on the substrate, or on nearby electrodes immersed in the plasma. A Particle-in-Cell simulation with Monte Carlo Collisions (PIC-MCC) was conducted of the application of DC voltage steps (and staircases) on an electrode, during the afterglow of a capacitively-coupled pulsed argon discharge, to control the energy of ions incident on the counter-electrode holding the wafer. Staircase voltage waveforms with selected amplitudes and durations resulted in ion energy distributions with distinct narrow peaks, having controlled peak energies and fraction of ions under each peak. A semi-analytical model was also employed to achieve "tailored" IEDs, i.e., distributions with a desired shape and energy spread (for example a nearly-monoenergetic IED with given FWHM). This was again accomplished by applying judicious voltage waveforms on the substrate electrode. Predicted IEDs were compared with experimental data. Strategies to control the energy flux of bombarding ions or to distribute the total ion energy flux to different energies were identified.

Work supported by DoE Plasma Science Center and NSF.

11:40am **PS-FrM11 Molecular Dynamic Simulation for Selective Etching of Silicon Nitride and Silicon Oxide by Hydrofluorocarbon Ions**, *R. Shigekawa, M. Isobe,* Osaka University, Japan*, M. Fukasawa, T. Tatsumi,* Sony Corporation, Japan*, S. Hamaguchi*, Osaka University, Japan

Selective etching of silicon oxide (SiO_2) over silicon nitride (SiN) has been widely used in microelectronics fabrication processes such as contact hole etching in self-aligned processes, formation of a stress liner, and dual/triple hard mask (DHM/THM) etching processes of dual-damascene structures. Opposite selective etching of SiN over SiO_2 with high selectivity would be also desirable for various processes. In general, when a fluorocarbon gas is used for etching processes, a carbon film tends to be accumulated on SiN surface, which is considered to reduce its etching rate. Therefore, there have been various attempts in plasma processing to increase the SiN etching rate by reducing carbon films over SiN with the use of hydrogen reactions with carbon. In such plasma processing, hydrofluorocarbon gases are typically used. In this study, we have performed molecular dynamics (MD) simulations of SiN and SiO_2 etching by CH_xF_y ions and compared their etching rates and surface chemistry, especially focusing on effects of hydrogen on the process. The reactive interatomic potential functions for atomic systems of Si, O, F, C, N, and H were developed in-house for the MD simulations code, based on atomic interaction data of small molecules in ground states obtained from ab-initio calculations. Details of the atomic potential functions used in the simulations will be presented elsewhere. Simulations are typically performed on a small block of a model substrate that consists of several thousand atoms and is subject to bombardment of energetic particles such as CH_xF_y. In the simulations, we evaluate sputtering yields, surface modification during the process, and characteristics of sputtered products. From the simulations, it has been found that hydrogen of CH_xF_y ions tends to reduce F accumulation on SiN surface, forming volatile HF, and sometimes promotes formation of cyanides such as HCN. Detailed simulation results, including sputtering yields and surface chemical compositions, will be given in this presentation.

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