Plasma Science and Technology Division
Room: 21 - Session PS+AS+SE-MoM

Atmospheric Pressure Plasmas

Moderators: Olivier Guaitella, Ecole Polytechnique - CNRS, France, Seiji Samukawa, Tohoku Univeversity, AIST, Japan

8:20am **PS+AS+SE-MoM1 Study of Atmospheric-pressure kHz Multi-jet Plasma System**, ***Vladimir Milosavljevic***, *J. Lalor, L. Scally, P.J. Cullen*, Dublin Institute of Technology, Ireland

Non thermal plasmas can be generated in laboratory conditions using generic, readily available and easily sourced components. Examples include glass tubing, copper or stainless wire electrodes, metal mesh, plastic enclosures, and step-up transformer based power supplies. Such sources, although effective, may not offer optimised conditions or efficiencies. In many cases they may not sustain extended operation due to excess thermal and electrical breakdown. Second-generation laboratory apparatus and scaled up designs involve selected materials, custom machined components, electrodes based on calculated requirements, and suitably designed or sourced power supplies. These assemblies will offer a more accurate theoretical and empirical view of the plasma performance. The inclusion of a material selection software tool for the rational selection of engineering materials can provide detailed information relating to the mechanical thermal and electric properties. Developing a non-thermal atmospheric plasma source involves three important factors for material selection. Firstly the application and operating conditions of the design needs to be examined; is it to be handheld, exposed to ambient air or contained in an enclosure. For many plasma sources, certain polymers offer an ideal material, for other configurations, composites or metals may be best. Secondly, does the source need to facilitate a controllable environment in which to generate the plasma, in other words, is it necessary to purge or evacuate the enclosure in order to accurately control the gas chemistry, if this is the case, a choice of material for this housing and containment area must be considered. The third factor is the material selection for the conducting elements, namely the cables, electrodes and grounding components. Typical electrode metals include copper, aluminium, brass and stainless steel.

In this work 12 circular plasma jets are presented. They are designed and built in-house, and power up with a single phase generator of 10-30 kV, at 10-100 kHz that powers up to 2 kW. Voltage-current measurements and optical emission spectroscopy (OES) are applied for optimization of transient discharges operated for several different gas chemistry at atmospheric pressure. The influence of applied voltage, frequency, gas flow rate and gas chemistry in relation with the OES signal, plasma plume formulation, gas velocity and electrical properties of plasma jets are the objectives of this study.

This work was funded under the 'PlasmaGrain' project funded by the SFI, Republic of Ireland.

8:40am **PS+AS+SE-MoM2 Synthesis of Nitrates by Atmospheric Microplasma Over Water : Effect of the Experimental Parameters and Intermediate Species**, ***Nicolas Maira***, *C. De Vos, F. Reniers*, Université Libre de Bruxelles, Belgium

Nowadays, nitrates are used mainly as fertilizers in agriculture. They are produced by the combination of the Haber-Bosch and Ostwald process. Industry, throughout the years, has increasingly optimized the energetic yield of this synthesis. Nevertheless, this method requires the use of a hydrogen source, essentially extracted from fossil fuel. Moreover, nitrates synthesized in colossal plant factories have to be shipped to the end-user. However, in some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly in a solution [1]. The mechanism of formation of nitrates using an atmospheric microplasma discharge operating in air or in argon in an open air environment is investigated. The effect of the treatment time, the discharge current and power, the water surface – capillary distance, and the solution pH on the formation of nitrogen oxides in the gas phase and in solution is studied. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

The total amount of NO_x formed in a solution shows a linear trend with the total charge injected into the plasma with however different slopes for nitrites (NO_2^-) and nitrates (NO_3^-). The reaction mechanism involves the formation of gas phase NO, as evidenced by OES. It is known that the synthesis of nitrates is pH-dependent [2]. In an acidic solution with a pH below 3, the formation of nitrates is favored whereas a higher pH allows the formation of nitrites which are oxidized in nitrates after the treatment. The transformation of nitrites into nitrates after plasma synthesis is monitored by IC during time and seems to follow a logarithmic trend. The performed experiments allow the determination of the amount of energy required to form a mole of nitrate in this set-up.

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9:00am **PS+AS+SE-MoM3 Plasma Catalysis for CO_2 and CH_4 Conversion at Atmospheric Pressure**, *A. Ozkan, S. Chorfi, L. Brune, T. Visart de Bocarmé*, ***François Reniers***, Université Libre de Bruxelles, Belgium

The field of plasma-catalysis, i.e. combining a plasma process and a catalyst, either inside the plasma or in its post-discharge is gaining importance for the conversion of CO_2 and CH_4 mixtures. Indeed, the combination of plasma and catalysis could not only increase the conversion of these gases, but also orient the reaction(s) towards the synthesis of valuable molecules.

This paper will present first the main factors that influence the conversion and the energy efficiency for the reduction of CO_2 using an atmospheric pressure dielectric barrier discharge. Second, an alumina supported catalyst will be added between the electrodes and its effects on the conversion of pure CO_2, pure CH_4 and CO_2/CH_4 mixtures will be presented. Ni, Co, Cu have been tested, as well as various loadings of Ni.

The conversion is studied by atmospheric mass spectrometry, and the chemical identification of the end products was obtained either by mass spectrometry or gas chromatography.

It is shown that the frequency, the pulse mode, the dielectric nature and thickness strongly influence the conversion and energy efficiency of the reaction, whereas the residence time and the power injected into the discharge modify the conversion[1]. An increase in the Ni loadings leads to an increase in conversion of both CO_2 and CH_4. If CO and H_2, starting molecules for more complex organic chemistry, are always the main products of reaction, C2, C3 and C4 molecules, oxygenated or not are also detected. The effect of the nature of the catalyst on the relative amounts of these molecules is discussed.

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9:20am **PS+AS+SE-MoM4 Aluminium Surface Plasma Treatment at Atmosphere Pressure**, ***Lucia Bonova***, *I.A. Shchelkanov, C. Ahn, S. Chaudhuri, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Plasma surface treatment at atmosphere pressure is a fast growing industry. Among other applications, surface treatment of metals for adhesion and corrosion resistance improvement has attracted widespread interest. Being operated at atmosphere pressure, various types of plasma discharge devices provide efficient, cheap and large scale processing capabilities. In this area, surface treatment of aluminium for surface properties modification is of great interest as it can decrease steps in process for final coating deposition, reduce usage of harmful chemical reagents, which in their turn require costly dispose procedures, and increase functional coatings performance.

The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device and a method for multicomponent metal coatings deposition at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. The device is capable of coating deposition from a solid metal state and from gas carried precursors as well as composites with processing gas like ZrO. These capabilities make ECAP a very flexible tool for gradient coating deposition for surface functionalization and adhesion improvement. In this gradient coating, the alumina facing materials is gradually replaced with a second layer material with perfect adhesion for final functional coating.

Current work discusses several methods, which were used to improve aluminium surface wettability and adhesion to an epoxy. As a fundamental experiment, we have conducted the simple treatment on aluminium plate by ECAP which operated with feedstock gas of evaporated H_2O and He. It shows remarkable enhanced epoxy adhesion on aluminium sample against the

control condition. System configuration for roll-to-roll applications and broad area coatings/cleaning are also discussed.

9:40am **PS+AS+SE-MoM5 The Role of Bulk Liquid Transport Processes in the Plasma-Liquid Interfacial Chemistry**, ***Selma Mededovic Thagard***, *M. Vasilev, D. Bohl, P. Conlon*, Clarkson University **INVITED**

Plasmas formed directly in and contacting a liquid are powerful sources of reactive radicals, ions and high-energy electrons and have been successfully used to sterilize water and fruit juices, purify water, synthesize materials and nanoparticles, and for applications in plasma medicine, electrical transmission, and polymer surface treatment. Nevertheless, despite the obvious versatility in processing capabilities, the optimization and broader application of electrical discharge plasmas in and contacting a liquid have been limited due to a general lack of understanding of the underlying physical and chemical processes occurring at the plasma-liquid interface. Despite the significant progress that has been made towards understanding interfacial chemistry of plasmas in the last decade or so (especially for air plasmas contacting water), relative contributions of plasma processes such as formation and diffusion of reactive species and bulk liquid processes such as electrohydrodynamic flow to interfacial dynamics have not been yet determined.

This work investigates the extent to which bulk liquid processes, primarily bulk liquid composition and plasma-induced electrohydrodynamic flow control the rates of chemical reactions at a plasma-liquid interface. We have determined the efficacy of the plasma process for treatment of a wide range of different compounds and used the results of this investigation to construct a model to predict the approximate treatability of any compound based on just a few of the compound's physical properties. Experiments with different initial bulk liquid concentrations of non-surfactant and surfactant compounds have also been performed to investigate how interfacial compound concentration affects its removal rate. Particle Image Velocimetry has been used to quantify the surface velocity of a liquid as a function of its chemical composition.

10:40am **PS+AS+SE-MoM8 Efficiency of Electrolytic Reduction of Aqueous Metal Salts to Metal Nanoparticles at a Plasma-Liquid Interface**, *S. Ghosh*, ***Ryan Hawtof***, Case Western Reserve University, *P. Rumbach, D.B. Go*, University of Notre Dame, *R. Akolkar, R.M. Sankaran*, Case Western Reserve University

Electrolytic cells with a plasma serving as one or both of the electrodes eliminate the solid metal and allow electrochemical reactions to be carried out at a gas-liquid interface. This is particularly beneficial for the synthesis of metal nanoparticles from metal salts since the deposition of a thin film onto the electrode is avoided. However, because of the complexity of the plasma and the resulting interfacial reactions, the mechanism for metal nanoparticle formation remains unknown.

Here, we designed experiments to understand the mechanism of the reduction of silver nitrate ($AgNO_3$) to silver (Ag) nanoparticles by a previously reported atmospheric-pressure, direct current microplasma operated as the cathode. We applied a well-known methodology in electrodeposition to assess the faradaic efficiency whereby the mass of the synthesized material is compared with the theoretical amount of mass estimated from the charge injected into solution. A faradaic efficiency of 100% would indicate that all the charge is going towards the desired reduction of Ag cations to solid Ag, $Ag^+ + e^- \rightarrow Ag^0$, whereas an efficiency less than 100% would suggest that there are side reactions, most probable of which is the second order recombination of (solvated) electrons to form hydrogen gas and hydroxide ions, $e^-_{(aq)} + e^-_{(aq)} + 2H_2O_{(l)} \rightarrow H_{2(g)} + 2OH^-_{(aq)}$.

We find that at a relatively high $AgNO_3$ concentration in the bath, the faradaic efficiency depends weakly on the current, reaching values of 100% at 2 mA and decreasing to slightly less than 100% at 6 mA. To corroborate these measurements, the mass change of a Ag foil anode which oxidizes in solution by the reverse of the cathode reaction, $Ag^0 \rightarrow Ag^+ + e^-$, was compared and found to yield slightly lower efficiencies, but with the same overall trend. At constant current and varying $AgNO_3$ concentration in the bath, the faradaic efficiency was found to drastically decrease to less than 100%. We interpret these results as follows. The kinetics of the primary reactions, Ag^+ reduction and second order recombination, depend on the respective rate constants which are similar (3.7×10^{10} M/s and 5.5×10^9 M/s) and the reactant concentrations. At low current or high $AgNO_3$ concentration, the rate of Ag^+ reduction is higher than second order recombination and the faradaic efficiency approaches 100%. Conversely, the rate of second order recombination is higher than Ag^+ reduction at high current or low $AgNO_3$ concentration, lowering the faradaic efficiency. A reaction model was developed to support these interpretations.

11:20am **PS+AS+SE-MoM10 Amorphous Indium Zinc Oxide (IZO) Semiconductor Films Grown by Atmospheric Plasma-Enhanced Spatial ALD for Application as High-Mobility Channel in Thin Film Transistors**, *A. Illiberi, I. Katsouras, S. Gazibegović, B. Cobb, E. Nekovic,* TNO-Holst Centre, Netherlands, *W. van Boekel, C. Frijters*, TNO-Solliance, Netherlands, *J. Maas*, TNO-Holst Centre, Netherlands, ***Fred Roozeboom***, TNO-Holst Centre & Eindhoven University of Technology, Netherlands, *Y.L.M. Creyghton*, TNO-Solliance, Netherlands, *P. Poodt*, TNO-Holst Centre, Netherlands, *G. Gelinck*, TNO-Holst Centre & Eindhoven University of Technology, Netherlands **INVITED**

Less than a decade ago, InGaZnO has been reported as a new Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels [1]. Among these, indium zinc oxide (IZO) is emerging as the most promising AOS candidate for next-generation displays based on oxide TFTs because it combines a very high electron mobility with excellent optical transmission and thermal stability [2,3].

We have grown InZnO thin films by plasma-enhanced spatial atomic layer deposition (s-ALD) [4,5] and these layers have been manufactured into oxide TFT and ring oscillator devices which outperform the state-of-the-art. We will describe the growth of InZnO at atmospheric pressure and high deposition rates (~ nm/sec) starting with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special atmospheric plasma source design of the so-called Surface Dielectric Barrier Discharge (SDBD) type [6]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapors, the In/(In+Zn) ratio of the film can be accurately tuned over the entire composition range from zinc oxide to indium oxide. TFT test devices with an In/Zn ratio of 2:1 show very high field-effect mobility exceeding 30 cm^2/V.s (Fig. 1), excellent thermal (Fig. 2) and bias stress stability. We will further demonstrate the scalability of the IZO TFTs by fabricating 19-stage ring oscillators operating at 200 kHz which outperform the state-of-the-art.

This superior electrical performance, in combination with the intrinsic advantages of spatial ALD demonstrate the great potential of this atmospheric plasma concept for application in commercial manufacturing of low-cost and large-area AOS-based electronics.

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Plasma Science and Technology Division
Room: 23 - Session PS+AS-MoM

Plasma Processing of Challenging Materials
Moderators: Erik V. Johnson, LPICM, Ecole Polytechnique, France, Osamu Sakai, The University of Shiga Prefecture

8:20am **PS+AS-MoM1 Control of Plasma Doping Conformality in FinFET Arrays**, ***Mona Ebrish***, *O. Gluschenkov*, IBM Research Division, *M.J.P. Hopstaken*, IBM T.J. Watson Research Center, *F. Torregrosa*, Ion Beam Services

FinFET devices are rapidly emerging as a standard transistor architecture for extending CMOS scaling beyond the 22 nm technology node because of superior electrostatic channel control. One practical challenge is to achieve a high degree of conformality for source/drain (S/D) extension doping along the Fin sidewalls. Conformal extension doping is crucial to minimize finFET series resistance while maintaining electrostatic channel control. Precise control of transistor characteristics over large-scale CMOS circuits and systems mandates that the extension doping and its conformality be maintained over arrays of finFETs with tight fin pitch. Plasma doping, with its wide distribution of impinging ion angles, provides an alternative to conventional ion beam implantation for fin array sidewalls. The traditional

1D Secondary Ion Mass Spectrometry (SIMS) depth profiling technique is unable to quantify the doping profiles in fin array sidewalls and hence the 1.5D SIMS approach (SIMS through array of fins) is used in this study. The retained sidewall dose measured by 1.5D SIMS is compared to a predicted number of impinging plasma ions that arrive to the fin array with certain angle and energy distributions dependent on the plasma conditions. This comparison takes into account the impinging ion cut off angle caused by adjacent fin shadowing in tight-pitch arrays. Based on those findings, a tuning of the plasma conditions was applied to obtain better than 50% dopant uniformity along the Fin sidewalls. The ability to control impinging ion angle distributions in plasma doping provides a valuable tool for improving doping conformality in tight-pitch fin arrays.

8:40am **PS+AS-MoM2 Study of Plasma-etching Parameter Impacts on Two-dimensional Electron Gas Degradation in AlGaN/GaN Heterostructures**, ***Frédéric Le Roux***, *P. Burtin, N. Possémé, A. Torres, S. Barnola*, CEA-Leti, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructrures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors and diodes.

Today, plasma-etching are considered as one of the most critical step in fabrication of such devices. Indeed plasma etching can lead to charge generation (depleting the channel)[1,2], AlGaN amorphisation (modifying the structure and the polarisations of the AlGaN)[3,4] or element implantation inducing charges or traps[5].

In this study, we propose to evaluate the impact of several plasma parameters (chemical, physical and physico-chemical) on 2DEG degradation occurring during silicon nitride etching (selectively to AlGaN). Experiments have been carried out on 200mm wafers using the following stack: 10nm Si_3N_4/24nm $Al_{0,22}Ga_{0,78}N$/AlN spacer/2µm GaN/buffer layers. The AlGaN degradation has been determine thanks to Rsheet and Hall measurements.

First the impact of a conventional fluorocarbon etch chemistry ($CF_4/CH_2F_2/O_2$/He) on 2DEG degradation will be presented as an ion-energy function. It will be demonstrated that Rsheet is degraded with the ion energy increase and confirmed by the evolution of career- density and mobility.

Then the pure-chemical etching effects (using wet and downstream-plasma etching process) as well as physical etching effects, with ion bombardment, (using Ion Beam Etching process (IBE)) will be discussed in term of Rsheet.

Finally, the benefit of new silicon nitride etching process, which has already been tested and validated for silicon nitride spacer application[6], has been evaluated for diode contact application. This process is based on two steps. In a first step, the film is modified in volume by a He plasma performed in a conventional etch tool (ICP) followed by a second step of selective removal (HF dip) of the modified layer (Si_3N_4) with respect to the non-modified material (AlGaN).

Thanks to this study, the plasma-etching's role in the channel characteristics degradation have been highlighted and linked to the plasma parameter through the Rsheet and Hall measurement evolutions. In order to increase the degradation mechanism understanding engendered by etching steps, physico-chemical characterisations will be developed to determine the degradation sources.

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9:00am **PS+AS-MoM3 Spatiotemporal Non-uniformity of CVD Plasmas and Film Qualities**, ***Masaharu Shiratani***, Kyushu University, Japan **INVITED**

Here we discuss great impact of nanoparticles formed in CVD plasma on uniformity of the plasma and film qualities [1-5]. Uniformity of thickness, composition, structure, and properties is a major concern of plasma CVD films. Multiple precursors including radicals, ions, and nanoparticles contribute to the film formation and hence their flux and flux ratio to the surface determine the film uniformity. Although most studies and text books describe film formation due to radicals and ions, such precursors are predominant only for very low pressure (< 5 Pa); in a pressure range of 10-500 Pa for most plasma CVD, contribution of nanoparticles to the film volume is 10-60% and cannot be disregarded [1-3]. CVD plasma tends to have inherently spatiotemporal non-uniformity of its internal parameters mainly because of nanoparticles. Nanoparticles have long time constant of their nucleation and growth. They tend to be charged negatively and are trapped in plasma. Nanoparticles act as loss sites of electrons, ions, radicals, and nanoparticles; and hence they have great influence on non-uniformity of plasma parameters, deposition rate, and film qualities. Particularly, they tend to give nonlinear response of CVD plasma, such as hysteresis, to discharge power and pressure. We show a model which reproduces well such non-linear response, and contribution of nanoparticles is one of keys to realize uniformity of high quality films [4, 5]. There is plenty of room to improve qualities of plasma CVD films by paying attention to contribution of nanoparticles to the films.

Work partly supported by JSPS KAKENHI grant numbers 26246036 and 16K13922.

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9:40am **PS+AS-MoM5 Surface-driven CH_4 generation from CO_2 in Low-pressure Non-thermal Plasma**, ***Kazunori Koga***, *S. Toko, S. Tanida, M. Shiratani*, Kyushu University, Japan

The methanation of CO_2 attracts attention as the way to produce rocket propellant fuels at Mars because CO_2 comprises 95% of the atmosphere of Mars and water exists on Mars [1]. This reaction is called the Sabatier process and has been studied using catalysts under high pressure over 1 atm and high temperature above 200 ºC to realize a high conversion efficiency. However, the pressure on Mars is 135 times smaller than that of the Earth, and the average temperature is extremely low of -63 ºC [2]. A method using low-pressure non-thermal plasma allows methanation under low pressure and low temperature conditions [3]. Therefore, the plasma process is suitable for methanation at Mars. Here, we converted CO_2 to CH_4 using a capacitively coupled plasma (CCP) together with Cu catalyst. Experiments were carried out using a CCP reactor, excited at a frequency of 60 MHz. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The electrode material was Cu. CO_2 gas flow rate was 1.0 sccm and that of H_2 was 6.0 sccm . The pressure was 750 Pa and the temperature was room temperature. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. CH_4 yield depends on surface condition of Cu electrodes, indicating that surface reactions on Cu electrodes dominate the CH_4 generation. Moreover, CH_4 generation has a long time constant more than 500 s, whereas CO_2 conversion has a short time constant of 80 s. These results indicate that CO_2 conversion takes place in gas phase by electron impact dissociation, while CH_4 generation involves several reaction steps. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

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10:00am **PS+AS-MoM6 Plasma Modification of Carbon Fibres for Tough Carbon Fibre Composites**, ***Sally McArthur***, *R. Radjef, BL. Fox*, Swinburne University of Technology, Australia

Carbon-fibre manufacturing is a well established process that includes a surface treatment and a sizing step which are fast and easily incorporated into the production process. In the electrolytic oxidation steps, ammonium bicarbonate is used to introduce functional and polar groups to the surface while weakly bound basal planes are removed and the surface roughness is increased. All these are desired effects that are then covered with the application of the sizing layer, which protects the fibre surface during subsequent processing steps. The size is generally an epoxy based emulsion that provides handleability, lubrication, protection and is supposed to create a strong bond. This production process creates a complex multilayered interphase that is not well understood. It is believed that the size partially reacts with the surface functional groups, leaving a sizing layer that is depleted in epoxide groups and hence not able to fully cure. Furthermore how do we know that enough hardener diffuses through the matrix to the fibre surface to fully cure the sizing layer in the first place?

The aim of this study is to replace the current surface treatment and sizing step by a two-step plasma approach that allows the formation of a controlled interphase. In part one of this project a comparative study between electrolytic oxidation and air plasma treatment has been performed. In a second stage plasma polymerisation of TMDSO was used to produce films of variable mechanical properties by controlling the plasma power. This talk will focus on the the development and characterisation of the lab-based plasma system used to deposit uniform coatings onto the carbon fibres using a reel-to reel process and dual electrode array.

10:40am **PS+AS-MoM8 Damage Free Plasma Etching Processes of III-V Semiconductors for Microelectronic and Photonic Applications**, ***Erwine Pargon***, *M. Bizouerne, C. Petit-Etienne, L. Vallier, G. Gay, M. Fahed, K. Rovayaz, M. Fouchier, C. Bellegarde, V. Renaud, G. Cunge, O. Joubert*, CNRS-LTM, Université Grenoble Alpes, France, *E. Martinez, N. Rochat*, CEA-Leti, France **INVITED**

Due to their inherent advantages of direct bandgap and high electron mobility, III-V semiconductor materials are today widely used as active materials for a wide range of applications including high-speed and power electronic devices, and many types of opto-electronic and photonic devices. Recent progress in both molecular wafer bonding technology and monolithic heteroepitaxy let envisage the integration of III-V semiconductors directly on a Silicon platform. If successful, such integration paves the way for the emergence of highly performant devices, taking advantages of both III-V unique properties and the maturity of Si processing. Some promising examples are the use of high mobility III–V channel materials to extend the performance of Si CMOS, or the unification of electronics and photonics by combining photonic components with a silicon platform for next-generation optical interconnects. For all these future technologies, development of industrial processes for III-V semiconductors patterning is necessary. Plasma etching allows feature patterning with a nanometric control of the dimension, but one major drawback is the creation of defects in the vicinity of the etched surfaces, that can change the electro-optical properties of the semiconductor, and ultimately compromise the device performance. There is today a lack of knowledge on by which mechanisms and to what extent the plasma etching process induces damage at the III-V pattern sidewalls and the consequence it has on the device performance. The objective of this work is first to provide a better understanding of plasma-induced damage at the sidewalls of micro-nano-patterned III-V semiconductors by establishing a direct link between structural and chemical modifications induced by plasma etching, and opto-electrical properties. Based on such comprehensive know-how, the second objective is to provide technological solutions to minimize this damage in order to propose low damage plasma process compatible with the fabrication of commercial devices. The present study mainly focuses on the plasma etching process development of InGaAs used as a high mobility channel in a FinFET for microelectronic applications and of InGaAs/InP heterostructures used as a laser in hybrid photonic integrated circuits. Etching experiments are carried out in industrial ICP reactors. The structural damage induced at the pattern sidewalls (amorphization, stoichiometry, roughness..) are evaluated by electronic microscopies, AFM and nanoauger spectroscopy. The optical properties of the III-V semiconductors at the pattern sidewalls are analyzed by cathodoluminescence.

11:20am **PS+AS-MoM10 Fabrication of Metal Nanoparticle-dispersed Nanocomposite Films by *In Situ* Plasma Reduction of Metal Cation-containing Polymer Films**, *D.R. Boris*, Naval Research Laboratory, ***Souvik Ghosh***, Case Western Reserve University, *S.C. Hernandez*, Naval Research Laboratory, *C.A. Zorman*, Case Western Reserve University, *S.G. Walton*, Naval Research Laboratory, *R.M. Sankaran*, Case Western Reserve University

Nanocomposites composed of inorganic nanoparticles and polymers have broad applications because of their unique combination of optical, electrical, thermal, and mechanical properties. A key fabrication challenge is dispersion of the two different phases which leads to separation and particle agglomeration. Compared to mixing premade nanoparticles with polymers, *in situ* formation of nanoparticles from a thin film containing the metal precursor and polymer has the potential to improve dispersion. Various approaches to reacting the metal precursor have been explored including heat treatment, UV exposure, and chemical processing. Low-temperature plasmas are particularly unique due to their inherent compatibility with temperature-sensitive polymers, and potential for rapid large-area processing. However, the mechanism for plasma-driven particle formation remains poorly understood.

Here, we carry out a systematic study of *in situ* plasma reduction of metal-cation containing polymer films to form nanoparticle-dispersed nanocomposites. Films were prepared from solutions of silver nitrate ($AgNO_3$) and polyacrylic acid (PAA). Chelation of the polymer with the metal cation produced a precipitate that was collected by centrifugation and cast as a thin film. The films were then exposed to a low-pressure, electron-beam generated plasma operating over a broad set of conditions aimed at delivering a controlled flux of low-energy argon ions. The as-treated films were analyzed with UV-visible absorbance spectroscopy and scanning electron microscopy (SEM). Absorbance confirms the presence of the localized surface plasmon resonance (LSPR) for Ag nanoparticles. The spectra show significant changes in the peak intensities with negligible shifts in the peak wavelength with plasma process changes, indicating that the particle concentration increases or decreases with a relatively constant average particle size. We correlated these changes in particle concentration to the variation in charge fluence at the film surface.

This work is partially supported by the Naval Research Laboratory base program and the National Science Foundation under Grant No. SNM-1246715.

Plasma Processing for Biomedical Applications Focus Topic
Room: 12 - Session PB+BI+PS-MoA

Plasma Agriculture & Processing of Biomaterials
Moderator: Kristian Wende, INP Greifswald

1:40pm **PB+BI+PS-MoA1 Control for Plant Disease and Development by Atmospheric Pressure Plasma**, ***Gyungsoon Park***, Kwangwoon University, Republic of Korea **INVITED**

Previously, we observed that seeds contaminated with *Fusarium fujikuroi* (a fungus causing rice bakanae disease) were more effectively disinfected in water by arc discharge plasma than ozone. Efficiency of disinfection was decreased when the distance between seeds and electrodes becomes greater. This indicates that shockwave from arc plasma may play an important role in seed sterilization, and we measured about 50-60 atm shockwave pressure. In addition, seed surface became more hydrophillic after plasma than ozone treatment indicating that water containing ROS and RNS can more easily get inside hull. Ozone level in water was decreased when seeds were present. This is probably due to the chemical reaction of ozone with seed surface molecules and will eventually cause the decrease in efficiency of seed disinfection. We also analyzed the effect of water and buffer treated with microwave plasma generated gas containing nitric oxide (PGNO) on development of spinach. The real time level of nitric oxide in water and phosphate buffer was increased to about 100 μM after treatment with PGNO for 50 min. Spinach treated with PGNO water seems to become more tolerant to drought stress. Our work was supported by the National Research Foundation of Korea (NRF) grant (No. 2010-0027963), Rural Development Administration (RDA) grant (No. PJ009891) and National Fusion Research Institute (NFRI) grant.

2:20pm **PB+BI+PS-MoA3 Biomass Pyrolysis Using Low Temperature Plasma**, *Y. Gao, N.B. Uner, J. Meyer, M. Foston,* ***Elijah Thimsen***, Washington University in St. Louis

Low temperature plasmas (LTP) are recently being used for processes involving complicated heterogeneous chemistry. Due to their unique non-equilibrium environment and the abundance of reactive radicals, LTPs are expected to bring selectivities and reactivities that are difficult to obtain in systems governed by local thermal equilibrium. In this study, we utilize low temperature plasmas for converting biomass into more valuable chemicals.

Biomass is an abundant and renewable source of carbon. It is recently reported that biomass can be supplied and processed at a scale large enough that is comparable to petroleum [1]. Current research efforts are focused on upgrading biomass into hydrocarbons and valuable aromatic compounds. One common method is to pyrolyze biomass into oils at high pressure. However, the product distribution usually turns out to be very broad, therefore the yields of the desired components are often low. Another common method is to gasify the biomass into syngas, a mixture of CO and H_2. Both pyrolysis and gasification are indirect routes of converting biomass into valuable chemicals. Complicated additional steps are usually required, as in the case of hydrodeoxygenation of pyrolysis oil or production of various paraffins/olefins via Fischer-Tropsch synthesis from biomass-derived syngas. Furthermore, a common drawback for both pyrolysis and gasification methods is the deactivation of catalysts due to coke formation.

In this study, we demonstrate a single-step process without catalysts that generates oxygen-free hydrocarbons with high yield. We will report low temperature plasma conversion of lignocellulosic biomass in a gram-scale radio frequency reactor. Preliminary work shows that the plasma rapidly converts solid feedstock into primarily small chain hydrocarbons. Effects of process parameters such as plasma power, plasma gas composition, operating pressure and biomass feedstock will be presented, along with a techno-economic analysis of the process.

[1] U.S. Department of Energy, "2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy," Oak Ridge National Laboratory, Volume 1, 2016.

2:40pm **PB+BI+PS-MoA4 Growth of Plasma-Treated Corn Seeds under Realistic Conditions**, ***Chisung Ahn***, *I.A. Shchelkanov,* University of Illinois at Urbana-Champaign, *J. Gill,* AgReliant Genetics, LLC, *D.N. Ruzic,* University of Illinois at Urbana-Champaign

Plasma treatments of agricultural seeds have been proposed to enhance germination and improve growth rate by elimination of unwanted microbes, water absorption control, introducing functional groups or other effects. In particular, making a plasma-activated medium which has nitrogen as its main component can affect the efficiency of water use in the germination phase. There is also a remarkable complementary effect between plasma treatments and biological pre-treatment. To confirm the plasma effects seen in the lab scale, this work seeks to investigate a variety of seed treatments on an industrial agriculture scale.

In this study, various kinds of plasma were introduced for mass treatment of corn seeds to investigate the germination and growth effect. The seed utilized for the experiment is an elite 111 days yellow dent corn hybrid adapted to the US Midwest. Seven experimental treatments were evaluated: Control, Biological treatment only, Plasma Activated Water (PAW) treatment, Atmospheric Pressure DBD Plasma, Microwave Atmospheric Plasma, Vacuum Plasma and Just Vacuum. The corn seeds were treated uniformly by one-layer arrangement on each stage without burning or blackening by the plasma. Each treatment was performed on a total of 1800 corn seeds. Seed of each experimental condition were treated with the recommended rate of Poncho Votivo with Acceleron, a commercial biological seed treatment that helps protect the seeds from fungus, insects, and nematodes after planting. The 1800 seeds were divided evenly into three replications with 100 seeds planted for each replication at six unique locations across central Illinois. The results of germination, growth, and product yield over the 2017 growing season will be presented.

3:00pm **PB+BI+PS-MoA5 Advanced Control of Plasma Medical Devices**, ***David Graves***, University of California, Berkeley, *A. Mesbah, D. Gidon,* University of California at Berkeley

Atmospheric pressure plasma jets (APPJs) have widespread use in plasma medicine. This presentation aims to demonstrate the importance of using advanced control strategies for safe, reproducible, and therapeutically effective application of APPJs for dose delivery to a target substrate. Key challenges in advanced control of APPJs arise from: (i) the multivariable, nonlinear nature of system dynamics, (ii) the need to constrain the system operation within an operating region that ensures safe plasma treatment, and (iii) the cumulative, non-decreasing nature of dose metrics. To systematically address these challenges, we propose a model predictive control (MPC) strategy for real-time control of a radio-frequency APPJ in argon. To this end, a lumped-parameter, physics-based model is developed for describing the jet dynamics, and cumulative dose metrics are defined for quantifying the thermal and non-thermal energy effects of the plasma on substrate. The closed-loop performance of the MPC strategy is compared to that of basic proportional-integral control. Simulation results indicate that MPC provides a versatile framework for dose delivery in the presence of system disturbances, while fulfilling the safety and practical constraints of APPJ operation. In addition, we demonstrate the use of advanced control in experimental APPJ systems. Advanced control can lead to unprecedented opportunities for effective dose delivery in plasma medicine.

3:20pm **PB+BI+PS-MoA6 Fingerprinting Different Plasma Sources for Biomedical Applications**, ***Katharina Stapelmann***, North Carolina State University, *K. Wende,* INP Greifswald, Germany, *B. Offerhaus,* Ruhr University Bochum, Germany, *C. Verlackt,* University of Antwerp, Belgium, *C. Klinkhammer, F. Kogelheide, M. Havenith,* Ruhr University Bochum, Germany, *A. Bogaerts,* University of Antwerp, Belgium, *P. Awakowicz, J-W. Lackmann,* Ruhr University Bochum, Germany

Cold technical plasmas (CAPs) are under investigation in various fields of industry and medicine. First clinical trials using CAPs for wound healing show promising results. Preliminary results in other fields of plasma medicine, such as cancer treatment, offer promising findings as well. However, the interactions of technical plasmas with biological samples on a molecular level are only partly understood. CAPs generate complex chemical cocktails, having an impact on various biological structures [1]. The impact can vary betweeen different sources, e.g. by employing a DBD in air or a noble gas driven jet. A better understanding of the chemical reactions occuring would allow to tune and adapt plasmas for specific tasks. One prevalent impact of plasma on biological targets has been the chemical modification of thiol groups, which carry out various important tasks in the human body, such as cell signaling and protein structure formation. As thiols are involved in many regulatory and functional processes in tissues, an in-depth understanding of the impact of plasma treatment on thiols is highly relevant for a safe application of plasmas in medicine.

In order to get insight into these interactions, various thiol-containing model substrates, such as the amino acid cysteine and larger target substrates, were investigated with different plasma sources [2,3]. By using a standard target substrate, the impact of various plasma sources can be compared not by means of a physical characterization but by their chemical impact. Stepwise increase of sample complexity allows monitoring how thiols are affected by plasma treatment in an ever more complex environment. The combination of experimental evidence and MD simulations permit a comprehensive

overview of chemical processes induced by plasma treatment. This combined approach allows a more throughout investigation of modifications on a molecular level and helps to understand fundamental plasma chemistry processes. Furthermore, knowledge about the substrate chemistry enables the use of test substrates as bio-probes for the investigation of plasma chemistry in other industrial fields [4].

[1] Lackmann J-W and Bandow J E 2014 *Appl. Microbiol. Biotechnol.* **98** 6205-13

[2] Kogelheide F *et al* 2016 *J. Phys. D: Appl. Phys.***49** 084004

[3] Lackmann J-W *et al*. 2015 *J. Phys. D: Appl. Phys*. **48** 494003

[4] Offerhaus B *et al*. 2017, accepted in *Plasma Process Polym*.

4:00pm **PB+BI+PS-MoA8 Exploring Plasma Coatings Comprising Vertical Chemical Gradients and Multilayers for Biomedical Applications**, ***Dirk Hegemann***, *M. Vandenbossche, M. Heuberger*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

The common definition of "surface" includes surface atoms and molecules, practically extending at the most some three layers – typically one nanometer. This definition is justified by the fact that many surface properties related to symmetry breaking, such as chemistry, wettability or surface charge are determined by the top most surface layer. The common understanding is that this thin surface region also determines how molecules adsorb onto it. Far less explored are effects due to interactions with deeper subsurface layers, i.e. the region extending over several nanometers underneath the "surface". This subsurface region, however, might significantly contribute to molecular adsorption via long-range (i.e. few nm) interaction forces; mainly interactions with fixed dipoles, water structuring and Van der Waals interactions. A key factor to make use of these interaction forces thus lies in the hydration of the subsurface region.

Therefore, stable plasma polymer films made of siloxanes were designed that contain a hydrophilic nanoporous base layer terminated by a hydrophobic top coating, nominally 2-12 nm thick. As a model molecule, bovine serum albumin (BSA) was selected and its adsorption was studied on gradient coatings as well as reference coatings immersed in water or phosphate buffered saline (PBS). As a result, protein adsorption was reduced on hydrated hydrophobic/hydrophilic gradient coatings, while dry or dehydrated films show the same adsorption as the reference hydrophobic plasma polymer film.

Furthermore, double layers made of a terminal a-C:H:O plasma polymer layer (1-5 nm thick) on a-C:H:N base layers were investigated comprising a gradient in carboxylic-to-amino groups. Again conditions were selected to obtain stable plasma polymer films when immersed in aqueous environments. Adsorption using the green fluorescent protein (GFP) on different double layers and reference layers were examined. Enhanced protein adsorption was observed for the 1 nm thick terminal layer of a-C:H:O on a-C:H:N as compared to each reference layer.

Hence the vertical nanostructure of a functional surface implies an additional factor to control adsorption processes. Protein adsorption, selectivity and bioactivity can thus be controlled by using subsurface effects being an important finding for biomedical applications such as e.g. tissue engineering.

Plasma Science and Technology Division
Room: 23 - Session PS+AS+SS-MoA

Plasma Surface Interactions

Moderators: Michael Gordon, University of California at Santa Barbara, Ying Zhang, Applied Materials, Inc.

1:40pm **PS+AS+SS-MoA1 Exploring the Gas-Surface Interface in NxOy Plasma Surface Modification of Zeolite Materials for Environmental Applications**, ***Angela Hanna****, *E.R. Fisher*, Colorado State University

With increasing concern for environmental health and climate change, there is a greater need to explore fundamental reactivity of pollutant species. Improving the effectiveness of substrates used in vehicular emissions abatement hinges on the ability to discern the contributions of gas-phase species in surface reactions. Here, inductively-coupled N_xO_y plasma systems were investigated to determine relationships between precursor chemistry and gas-surface interface interactions with different substrates. Precursor chemistry was probed via gas-phase diagnostics; time-resolved optical emission data elucidated NO (g) and N_2 (g) production kinetics from N_xO_y source gases, whereas steady-state emission and absorbance data provide information on energy partitioning between different degrees of freedom (e.g. vibrational and rotational modes). Specifically, we have determined rotational (T_R) and vibrational (T_V) temperatures for N_2 ($B^3\Pi_g \leftrightarrow C^3\Pi_u$) and NO ($X^2\Pi \leftrightarrow A^2\ \Sigma^+$). T_R and T_V for both molecules show strong positive correlations with applied rf power, as well as a negative correlation with system pressure. T_V is significantly higher than T_R for both N_2 and NO, regardless of precursor, with T_V ranging from ~2000 K to >3000K and T_R having values between ~300 K and 1000 K. Ultimately, these data afford significant insight into increased understanding of molecule formation and decomposition pathways, as well as overall plasma chemistry in nitrogen and oxygen-containing plasma systems of interest to pollution abatement. Similarly, interface studies explored the influence of both non-catalytic (e.g. Si wafers) and catalytic (e.g. zeolites, Pt wire) substrates on the gas-phase chemistry in the same plasma systems. X-ray photoelectron spectroscopy and scanning electron microscopy analyses of surface oxidation and morphological changes resulting from plasma processing will be presented. Furthermore, we will describe plasma surface modification of zeolites, in both a static plasma reactor and a rotating drum reactor. Our holistic approach to employing diagnostics tools to characterize the plasma, the surface, and the gas-surface interface suggests a more thorough evaluation of plasma processing for N_xO_y emission control.

2:00pm **PS+AS+SS-MoA2 Effects of Ion induced Damages on Etching Characteristics of ITO Thin Films**, ***Hu Li***, *K. Karahashi*, Osaka University, Japan, *M. Fukasawa, A. Hirata, K. Nagahata, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

Micro-fabrication of transparent conducing oxides (TCOs), such as tin-doped indium oxide (ITO) and zinc oxide (ZnO), has been performed for optoelectronic devices such as solar panels and head-mounted liquid crystal displays. With the increasing demand of such devices, more efficient and more controllable fabrication technologies for patterning of TCOs are highly required. Reactive ion etching (RIE), which uses energetic reactive ions and typically allows high etch rates and high selectivity over hard masks, may be suitable for high-resolution pattering of TCOs. Hydrocarbon-based non-corrosive gases such as CH_4 and methanol have been used for RIE processes of TCOs. However, etching reactions and mechanisms of such processes have not been well understood. Therefore, the goal of this study is to clarify the mechanisms of RIE of TCOs by hydrocarbon-based plasmas.

In this study, sputtering yields of ITO were measured with the use of a mass-selected ion beam system, which allows the injection of only desired ion species with a specified incident energy into a substrate set in an ultra-high vacuum chamber. It has been found that the physical sputtering yield of an ITO film increases with pre-injection of energetic hydrogen (H) or helium (He) ions, which indicates that some atoms of the modified ITO film are less tightly bound and become more amenable to physical sputtering. The X-ray Photoelectron Spectroscopy (XPS) observation of ITO films pre-treated by energetic H or He ion injections has shown that the increase of the sputtering yield cannot be explained by the surface reduction of ITO films. In our preliminary study on ZnO, we have observed by Transmission Electron Microscopy (TEM) that the grain sizes of a ZnO film decrease after the film is exposed to energetic He ion injection. Therefore we surmise that grain sizes of ITO also similarly decrease and consequently the regions of grain boundaries increase after the film is pretreated by energetic H or He ions. By definition, atoms at grain boundaries are less tightly bonded with surrounding atoms than those in the crystalline bulk and therefore the increase of the grain boundaries is likely to contribute to the increase of the sputtering yield of the film.

2:20pm **PS+AS+SS-MoA3 Nitriding Process for Next-generation Semiconductor Devices by VHF (162 MHz) Plasma Source**, ***YouJin Ji***, *K.S. Kim, K.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, for low power and high performance of semiconductor devices, the gate oxide thickness is scaled down and gate line-width is reduced. As a result, the role of nitride layer on gate oxide has become crucial to prevent the penetration of boron through thin gate oxide. In addition, high step coverage characteristics that are applicable to fine line patterns in a semiconductor device are also demanded. To keep pace with these detailed requirements, nitriding processes of the deposited silicon oxide employing conventional 13.56 MHz plasma source and N_2 as the nitriding gas has been generally utilized. However, 13.56 MHz plasma is difficult to decompose N_2 gas sufficiently, therefore, the thickness and nitrogen percentage of the oxynitride layer obtained by nitriding process are limited. In addition, high temperature operation above 200 ^oC can also cause the degradation of the device. In this study, a VHF (162 MHz) multi-tile plasma source was used for the decomposition of N_2 gas and the effect of the plasma conditions of

*** Coburn & Winters Student Award Finalist**

VHF multi-tile plasma source on the nitridation of silicon oxide at room temperature was investigated. Using the VHF (162 MHz) plasmas, high density nitrogen plasmas with a low electron temperature and high vibration temperature were generated and, with these plasmas, dense oxynitride films with high nitrogen contents could be fabricated. Also, by controlling the plasma conditions, highly uniform oxynitride films with a high step coverage could be also obtained.

2:40pm **PS+AS+SS-MoA4 Defect Generation in Graphene Films by Low-Pressure Inductively Coupled Argon Plasmas Treatments**, *X. Glad, P. Vinchon, S. Boivin, G. Robert-Bigras,* ***Luc Stafford***, Université de Montréal, Canada

For many applications, graphene properties need to be tuned by post-processing techniques, such as plasma treatment. The latter is commonly used as a graphene doping method [1]. However, the decoupling of doping and damage mechanisms may be complex. Typically, damage studies on graphene are carried out using high-energy electron beams [2] or ion beams at energy above a few tens of eV [3]. Nonetheless, a few studies showed that plasma treatment may induce damage on graphite although incident ions transfer less energy to the graphite lattice than the energy threshold displacement (T_d = 15-20 eV) [4]. The literature is strongly lacking systematic and parametric experimental studies of the defects induced in graphene by non-reactive plasma with low-energy ions.

The aim of this study is to investigate the defect formation on graphene films by low-pressure argon inductively coupled plasmas in the very low ion energy range (< 15 eV). To do so, plasma parameters have been assessed by Langmuir probe (LP) and mass spectrometry to determine conditions of fixed ion fluence but different ion energy. Such conditions were obtained by increasing the pressure while lowering the applied rf power and adjusting the treatment time. Raman spectroscopy (RS) was then carried out on each treated graphene sample to evaluate and identify the damage generation.

Our results reveal two contributions on the defect generation: one proportional with the ion energy, the other with the gas pressure. LP and optical absorption measurements have been coupled with a collisional-radiative model to estimate the main energetic species power fluxes (ions, VUV photons, resonant and metastable states). It showed that the ion contribution is the dominant one for each condition. Thus, it seems that with lower ion energy and higher pressure, surface diffusion and redeposition processes become preponderant resulting in a higher density of amorphous carbon found on the graphene sheet, as evidenced by RS. The occurrence of this amorphous matter would explain the high intensity D/G band ratio observed, even at very low-ion energy. Preliminary results thus suggest that, to achieve graphene doping by mild plasma treatment, lower pressure is desirable since minimal production of amorphous carbon is observed.

[1]: A. Dey *et al., Appl. Phys. Rev.* **3** (2016).

[2]: J. Kotakoski, A. V. Krasheninnikov, U. Kaiser, and J. C. Meyer, *Phys. Rev. Lett.* **106** (2011).

[3]: O. Lehtinen, J. Kotakoski, A.V. Krasheninnikov, and J. Keinonen, *Nanotechnology* **22** (2011).

[4]: B. Rousseau, H. Estrade-Szwarckopf, A. L. Thomann, and P. Brault, *Appl. Phys. A: Mater. Sci. Process.* **77** (2003).

3:00pm **PS+AS+SS-MoA5 The Role of Plasma Species and Sample Composition on Dense Amorphous Carbon Layer Formation and Polymer Etching Behavior**, ***Adam Pranda***, *S.A. Gutierrez-Razo, Z. Tomova, J.T. Fourkas, G.S. Oehrlein*, University of Maryland, College Park

Numerous polymer etching models have been previously developed to correlate the structure or composition of the polymer to the plasma etching behavior[1]. A key assumption in these models is that the polymer structure remains homogenous as it is etched. For applications in photoresist pattern transfer, this assumption is not valid since high-energy ion bombardment results in the formation of a heterogeneous structure consisting of a 2-3 nanometer thick dense amorphous carbon (DAC) layer on the polymer surface which mediates the overall etch rate.

In this work, we experimentally examined several key plasma and sample parameters that impact the etching behavior for a set of model polymers and PR193 and PR248-type photoresist. These parameters include plasma composition, fluxes of incident species in the plasma, intensity of ion bombardment-induced surface modifications that affect the etching behavior, polymer chemical composition and molecular structure, along with UV and VUV sensitivity in a plasma environment. From our experimental work, we have found that the thickness and intensity of the DAC layer is highly dependent on the chosen plasma parameters and the polymer composition/molecular structure.

We compare various models of the etching behavior of a polymer based on parameters such as the polymer chemical composition/structure and the flux of incident species in the plasma relative to experimentally observed relationships. Of key significance is the relationship between reactive plasma species and the state of the DAC layer.

One of the experimental correlations we have identified is that a molecular structure consisting of a greater ratio of carbon carbon-type bonding results in a more optically dense DAC layer, which limits the ion flux that reaches the bulk layer, and thus leads to a lower steady-state etch rate. In the presence of any reactive species in the plasma, such as oxygen or fluorocarbon, there is an additional component to the etch rate due to chemical sputtering which results in an increase in the etch yield of the DAC layer. Once the DAC layer is sufficiently depleted, the ion flux reaching the bulk layer increases and thus the bulk etch rate increases as well. Utilizing the experimental results, we seek to arrive at an etching model that can be applied in the development of new photoresists that attain a target steady-state etch rate.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

1. Oehrlein, G. S. et al. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.***29,** 10801 (2011).

3:20pm **PS+AS+SS-MoA6 Control of Ion Energy Distributions on Insulating Surfaces**, ***Tyler List***, *T. Ma, V.M. Donnelly, D.J. Economou*, University of Houston

A method for controlling ion energies on insulating substrates using pulsed plasma is presented. A synchronous bias voltage was applied to a boundary electrode in the afterglow of a pulsed plasma, resulting in a positive ion flux to the insulating substrate. To avoid excessive charging of the surface, DC square pulses were periodically applied to the chuck holding the substrate, to attract an electron swarm to the surface and neutralize the surface charge. Surface potential measurements were used to validate the proposed scheme. The effect of pulse width, amplitude, and frequency on the resulting surface potential waveform was examined. A Retarding Field Energy Analyzer was used to measure the ion energy distribution. When corrected for the non-uniform charge distribution prevailing when the applied RF frequency is less than the ion sheath transit frequency, the IED was similar to that predicted by a mathematical model of the system. Etching of quartz discs and 1000 nm-thick SiO_2 films, thermally grown on Si wafers, was also performed. For both types of substrates, beyond an etching threshold, the etching rate increased linearly with the square root of chuck bias. No clear effect of the boundary electrode bias voltage on the etching rate was observed. The behavior of etching rate as a function of the (DC chuck bias) pulse width mirrored the dependence of surface potential on pulse width. Work supported by NSF and DOE.

4:00pm **PS+AS+SS-MoA8 Ultra-high Si_3N_4 to SiO_2 Selective Etching by Fluorocarbon Based Remote Plasma**, ***Chen Li***, University of Maryland, College Park, *T. Hofmann, K. Edinger*, Carl Zeiss SMT GmbH, *G.S. Oehrlein*, University of Maryland, College Park

Plasma etching processes capable of highly selective Si_3N_4 to SiO_2 removal are increasingly required in fabrication of current integrated circuit devices. We report fluorocarbon (FC) based remote plasma etching processes for Si_3N_4 and SiO_2 substrates using inductively coupled plasma (ICP) and electron cyclotron wave resonance (ECWR) plasma reactors. For the remote plasma operating conditions direct ion bombardment of the sample surface is prevented and etching is primarily due to chemical reactions by neutral radicals. Such conditions can be realized by either high processing pressure for a remote ICP source or a neutralization plate for an ECWR source. Combinations of fluorocarbon gases, e.g. CF_4, with O_2 and N_2 additives have been evaluated. Etching behavior and surface properties are monitored using *in situ* ellipsometry. Optical emission spectroscopy (OES) has been used to evaluate the plasma gas phase chemistry. We show that ultra-high Si_3N_4 to SiO_2 etching selectivity can be achieved under remote plasma conditions in both reactors, and that control of the feed gas chemistry plays a key role. As is well-known, low levels of O_2 increase oxidation of FC gases and atomic F generation, which leads to increasing Si_3N_4 etch rate, whereas for high O_2 levels the F concentration is reduced and surface oxidation takes place. For these F-rich remote plasma conditions, SiO_2 is hardly etched and Si_3N_4 to SiO_2 etching selectivity of 7 and 87 were observed for the ICP and ECWR system, respectively. The observed etching behavior will be discussed using surface chemical studies of Si_3N_4 and SiO_2 by vacuum transferred x-ray photoelectron spectroscopy (XPS).

4:20pm **PS+AS+SS-MoA9 Effect of Temporal Variation of Discharge on Photon-induced Interface Defects in Pulse-modulated Inductively Coupled Plasma**, ***Yasufumi Miyoshi***, *M. Fukasawa, K. Nagahata*, Sony Semiconductor Solutions Corporation, Japan, *K. Ishikawa, M. Sekine, M. Hori*, Nagoya University, Japan, *T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan

It is important to reduce photon-induced interface defects, which degrade the performance of electric devices. Ishikawa et al. reported that using pulse-

time-modulated plasma reduces UV photon-induced defects [1]. In this study, we investigated how temporal variation of the discharge affected these defects in pulse-modulated $Ar/CF_4/O_2$ inductively coupled plasma (ICP).

In this study, we varied the ICP source pulse frequency (0.5–20 kHz) and duty ratio (50–100%) as well as the gas ratio of Ar/CF_4. To investigate the UV radiation damage, the interface-trap density (D_{it}) was measured by using on-wafer pallet for plasma evaluation (PAPE) [2]. We used D_{it}, which is proportional to the UV fluence from discharge, as an indicator of UV damage. Temporal changes in the optical emission spectroscopy (OES) intensity of pulsed plasma were also investigated.

The measured D_{it} was lower than that in the CW at lower frequencies but was higher at higher frequencies (> 10 KHz). Increasing the frequency increased D_{it}, which reached a maximum at 10 kHz for $Ar/CF_4 = 1$, and then decreased D_{it}. Using a lower CF_4 ratio shifted the maximum D_{it} to a lower frequency.

This frequency-dependent behavior comes from the transient behavior of the pulsed ICP. Time-resolved OES revealed an optical emission overshoot after ignition caused by the variation in the electron temperature and number density in the early ON phase. The number of overshoots increased with increasing frequency, increasing the UV fluence and D_{it}. At higher frequencies, the variation in the electron temperature and number density were suppressed due to stepwise ionization from residual long-lived metastable species in the early ON phase [3]. This behavior considerably decreased overshoot amplitude, in turn decreasing the UV fluence and D_{it}. At the lower CF_4 ratio, quenching of the metastable species by CF_4 decreased and the lifetime of the metastable species during the OFF phase likely increased. Therefore, we presume that, at the lower CF_4 ratio, the overshoot amplitude began to decrease at a lower frequency than when $Ar/CF_4 = 1$ and the maximum D_{it} consequently shifted to a lower frequency.

These results show that controlling the temporal variation of a pulse-modulated plasma is essential to reduce the photon-induced damage it causes during plasma processes.

[1] K. Ishikawa et al., J. Appl. Phys. **104** (2008) 063306.

[2] M. Fukasawa et al., Jpn. J. Appl. Phys. **52** (2013) 05ED01.

[3] S. K. Monfared et al., J. Phys. D: Appl. Phys. **46** (2013) 425201

4:40pm **PS+AS+SS-MoA10 Surface Mechanisms on Dielectric Surfaces Exposed to Low Pressure Glow Discharge and Atmospheric Pressure Plasma Jets**, ***Olivier Guaitella***, *A.S. Morillo-Candas*, Ecole Polytechnique - CNRS, France, *A. Sobota*, Eindhoven University of Technology, The Netherlands, *E. Slikboer, D. Marinov*, Ecole Polytechnique - CNRS, France, *B. Klarenaar, R. Engeln*, Eindhoven University of Technology, The Netherlands, *V. Guerra*, Instituto Superior Tecnico, Lisbon, Portugal **INVITED**

New applications of Non Thermal Plasmas (NTP) at atmospheric pressure such as biomedical applications, air treatment or CO2 recycling are growing rapidly with the better control of these plasma sources. All these applications rely on the effect of a transient plasma discharge with complex surfaces such as porous catalyst or biological tissues for instance. The interaction of plasma with surfaces is always a very challenging topic because of the multiplicity of phenomena modifying the surface but also because of the reverse influence of the substrate on the plasma properties. Therefore most of the studies dedicated to plasma surface interactions are performed with very low pressure plasmas and ideal model surfaces. No conclusion can be drawn on surface mechanisms if the plasma in contact with the surface is not well characterized while being in contact with the surface of interest.

The originality of the approach we have developed consists in the utilization a low pressure (1-10 mbar) pulsed dc discharge for investigation of elementary processes on the surface of real catalytic materials that are also studied in atmospheric pressure DBDs.

The pulsed glow discharge allow us to measure the dynamic of plasma parameters (Electric field, Gas temperature, radical densities, vibrational excitation etc…) to give constraints to kinetics models allowing us to distinguish between gas phase reactions and the role of elementary surface processes such as O atoms recombination or molecule conversion on surface. Various diagnostics have been used in the gas phase including Doppler broadened TALIF (for O atoms density and gas temperature), or step scan FTIR (for vibrational temperature of CO_2 and CO). Infrared absorption is performed in transmission directly through catalyst pellets exposed to the same plasma to investigate adsorbed molecules.

In parallel, other diagnostics are being developed to obtain electric field, temperature profile and adsorbed species on surfaces exposed to atmospheric pressure plasma sources. A kHz plasma jet configuration is used for its reproducibility as a first model plasma source for studying ionization wave interaction with surfaces. Surface electric field, charge deposited and is obtained under controlled atmosphere from polarization technique based on Pockels effect. Infrared absorption in transmission through catalyst samples is also used under plasma jet exposure.

The use of reproducible plasma sources allowing the combination of gas phase diagnostics and in situ surface diagnostics gives a new perspective on the importance of surface processes even at elevated pressures.

Plasma Processing for Biomedical Applications Focus Topic
Room: 12 - Session PB+BI+PS-TuM

Plasma Medicine
Moderator: Katharina Stapelmann, Ruhr-University Bochum, Germany

8:00am **PB+BI+PS-TuM1 Spatial Distribution of Biological Effects Induced by Plasma Reactive Species**, ***Sylwia Ptasinska***, University of Notre Dame **INVITED**

Several *in vitro* and *in vivo* studies have been conducted in a variety of cancer cell lines that demonstrate the efficacy of cold plasmas in causing cell death since the advent of this new research area in the plasma physics community in 2010. Due to the complexity of both the plasma and biological systems, many questions must be answered to sharply improve our understanding of the physical, chemical, and biological processes underlying their interactions. However, since cold plasmas produce a cocktail of reactive oxygen species (ROS) and reactive nitrogen species (RNS), these species are believed to be key agents that can induce a number of biological effects, including impairment of cell substructures and even cell death. Moreover, cancer cells have proven to be more susceptible to damage by these reactive species than normal cells subjected to plasma exposure. The outcome of cell responses to plasma treatment has inspired the potential application of plasma as an effective and safe tool for novel cancer therapy. Our research focuses on investigations of nucleus DNA damage in cancer cells and bacterial inactivation caused by exposure to plasma reactive species. Initially, to detect ROS and RNS that reached the targeted biological systems we used semi-quantitative test strips, while to investigate biological effects in cells we used digital imaging or immunofluorescence microscopy. Recently, to obtain the high-resolved spatial distribution of DNA strand breaks we developed a workflow with algorithms for image analysis using CellProfiler and MATLAB, including background correction, cell segmentation, feature extraction, cell classification, and data visualization. This method well preserves the essential spatial information about cell distribution, which is critical because of the localized nature of the plasma jet treatment. By applying both supervised and unsupervised machine learning techniques to the images, we were also able to classify the cells according to different cell cycle phases, and thus obtain spatial information regarding plasma jet effects on cell cycle progression.

8:40am **PB+BI+PS-TuM3 Mechanisms of Cell Death in Prostate Epithelial Cells after Treatment with Low Temperature Plasma**, *J. Packer, A.M. Hirst, F.M. Frame,* ***Deborah O'Connell***, *N.J. Maitland*, University of York, UK

Low-temperature plasma (LTP) treatment of cancer cells have been explored for a variety of malignancies. These plasmas, operated at atmospheric pressure and close to room temperature, are efficient sources of reactive oxygen and nitrogen species (RONS), electric fields and photons, and can induce a variety of biological responses. There is an increasing clinical move towards focal therapy for more conservative management of prostate cancer, with reduced levels of common side effects such as incontinence and impotence compared with radical treatments, and promising outcomes. Low-temperature plasmas may offer such potential.

A dielectric barrier discharge jet, created within a glass tube surrounded by two electrodes (~ 6 kV applied sinusoidal voltage), with a helium plus 0.3% oxygen gas flow is used for these investigations. We have employed both purified tumour cells freshly extracted from prostate cancer patients, and matching, non-tumour cells from a distant region of the same prostate. Freshly isolated primary tumour cells acts as a near patient model, which has recently confirmed differences in pharmacological susceptibility as compared with 30 year old established cell lines.

Treatment of primary prostate epithelial cells with LTP resulted in sigificant cell death in both normal and cancer cells; and no significant selectivity observed, as commonly reported. In addition, most cells appeared to die via a necrotic mechanism, rather than apoptosis, maybe as a result of the mitochondrial toxicities of the LTP-activated reactive oxygen species (ROS). However, some autophagy was also detected, which has been shown to act as a salvage pathway for sub-lethally damaged cells.

To determine which of the multiple plasma activated bio-reactive species are responsible for the cytotoxicity, we have explored immediate and longer-term effects on gene expression, with a particular focus on oxidative responses, in multiple patient samples. Comparative studies in the established cell lines indicated a delayed and different response, highlighting that cell lines don't always reflect the response of primary cells. Expression of 84 genes (mRNA by RT^2 arrays from Qiagen) was assessed at multiple time points, after a 3 minute LTP treatment, and candidate genes/response pathways were identified. Immunofluorescence and western blotting were used to verify changes in protein expression. The response varied according to the clinical grade of the tumour (including a remarkable downregulation of 18 factors only seen in the highest grade tumours). All epithelial cells showed a stimulation of transcription factor-driven anti-oxidative response, as a potential resistance mechanism.

9:00am **PB+BI+PS-TuM4 Selective Antitumor Effect of the Plasma-Activated Medium Produced by Atmospheric Pressure Plasma with High Plasma Density**, ***Yohei Takahashi***, *Y. Taki*, Nikon Corporation, Japan, *K. Takeda*, Meijo University, Japan, *H. Hashizume, H. Tanaka, M. Hori*, Nagoya University, Japan

Recently, atmospheric pressure plasma has been widely developed for the applications on various fields, such as synthesis approaches, surface modification, sterilization, etc. Especially, cancer therapy using atmospheric pressure plasma is one of the most attractive applications. The culture medium irradiated with the atmospheric pressure plasma was called Plasma-Activated Medium (PAM), which exhibited the selective apoptotic cell death of cancer cells. In this study, we have demonstrated the antitumor effect of medium induced by irradiation of atmospheric pressure plasma with high plasma density and compared the cell survival between cancer and normal cells, which showed that the selective apoptotic cell death was achieved. Additionally, the basic diagnostics of the plasma and the analysis of the PAM were performed and the relation with the antitumor effects was discussed. The emission peak of OH radical ($A^2\Sigma$-$X^2\Pi$) was observed in the atmospheric pressure plasma. This transition is the intense systems emitted by low temperature plasmas containing even a small amount of H_2O. The selective apoptotic cell death effect by treatment with PAM produced by atmospheric pressure plasma irradiation was confirmed. The survival of cancer cell after incubation in PAM was greatly lower than that of normal cell was. The productions of H_2O_2 and NO_2^- by irradiation of high density plasma were detected by the colorimetric assay. The synergistic effect of H_2O_2 and NO_2^- in PAM is considered to affect the proliferation of cancer cells.

9:20am **PB+BI+PS-TuM5 Multiplex Coherent Anti-Stokes Raman Scattering (CARS) Observations of HeLa Cells Cultured in Non-equilibrium Atmospheric Pressure-Plasma-Activated Medium (PAM)**, ***Kenji Ishikawa***, *R. Furuta*, Nagoya University, Japan, *K. Takeda, T. Ohta, M. Ito*, Meijo University, Japan, *H. Hashizume, H. Tanaka, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

Non-equilibrium atmospheric-pressure plasma (NEAPP) affects cancer cells not only directly[1] but also indirectly through exposure of cells to medium irradiated beforehand with NEAPP (i.e., plasma-activated medium [PAM]).[2] Recent studies have revealed that NEAPP irradiation generates reactive oxygen and nitrogen species (RONS) in the gas phase and relatively long-lived RONS such as hydrogen peroxide, nitrites and nitrates in the aqueous phase.[3] To further elucidate a cell-death mechanism in more detail, the present study focused on the direct analysis of PAM-induced intracellular molecules such as lipids, acylglycerol, triglyceride, adiposome in HeLa cells as cervical cancer cells. Lipid droplets (LDs) are dynamic organelles with complex and interesting biological functions that go beyond mere energy storage and are important in lipid homeostasis and metabolism. To evaluate LDs, coherent anti-Stokes Raman scattering (CARS) microscopy was used. The observation-results by multiplex coherent anti-Stokes Raman scattering (CARS) microscopy elucidated the mechanism underlying the apoptosis of HeLa cells in cultivating in PAM, leading to be simultaneously occurred the exhaustion of LDs in the cells in contrast to the accumulation, while the activation of caspase-3/7 was induced, though accumulation in lipid droplets (LDs) and lipid metabolism in the normal apoptosis of HeLa cells with activation of caspase-3/7 was previously reported.

Acknowledgement: This study was supported in part by the JSPS-KAKENHI (No. 24108002).

1 S. Iseki et al., Appl. Phys. Lett. **100**, 113702 (2012); 2 H. Tanaka et al., Plasma Med. **2**, 207 (2012); 3 N. Kurake et al., Arch. Biochem. Biophys. **605**, 102 (2016).

9:40am **PB+BI+PS-TuM6 Plasma Medicine - From Bench to Bedside**, ***Kai Masur***, *T. von Woedtke, K.D. Weltmann*, Leibniz Institute for Plasma Research and Technology, Germany

During the last decade it became possible to stimulate eukaryotic cells by applying non-thermal plasma. The same plasmas can be used to kill micororgansisms - both in vitro and in vivo. However, there is the need to understand the processes of how electrical fields, ROS /RNS and UV

generation influence the cellular activities in order to find the balance between stimulating or killing biological matter. Therefore, much effort had been done by in order to control the plasma components and finally modulate biological activities. It was shown before that argon plasma treatment leads in a time dependent manner to an activation of cell proliferation in human skin samples. Furthermore, it is known that non-thermal plasma is able to diminish bacterial load of cultured microorganisms *in vitro* independent of the strain. Even more, plasma reduces the amount of antibiotic resistant bacteria in the same manner as their non-resistant strains.

In 2013, new developed plasma sources were certified as medical products and since than those devises are in clinical application. Here we report on our findings on plasma treated chronic wounds and the efficacy of non-thermal plasma. There is a very promising rate of healed and improved wounds, which demonstrate that plasma indeed can help patients with chronic wounds. However, there are some discrepancies between *in vitro* findings and results from patient treatment. The bacterial reduction is lower than in *in vitro* studies, but skin regeneration seems not to be dependent on complete bacterial removal. On the other hand, patient treatment reveals new facts about the positive effects of plasma treatment of persisting wounds. Here we summarize the positive results of plasma mediated stimulation of patients with chronic wounds.

11:00am **PB+BI+PS-TuM10 Plasma Medicine, RONS, Tissue and Cell Models**, ***Rob Short***, University of Lancaster, UK, *E. Szili*, University of South Australia, Australia **INVITED**

Electrically-generated cold plasma gas discharges are being intensively researched for novel applications in medicine and biology. Significant attention is being given to the reactive oxygen and nitrogen species (RONS), initially generated upon plasma-air interactions that are delivered to biological systems. The effects of plasma exposure are observed deep within tissue, to millimetre depths and within cells. However, very little is known about the exact nature of the initial plasma-tissue interactions, including RONS speciation and delivery depth, or how plasma RONS intervene in biological processes. In this presentation I will focus on current research using tissue and cell models to learn more about the plasma delivery and transport of RONS into tissue and cells. I will argue this research is vital to establishing an underpinning knowledge that is needed to realise the full potential of plasma in medicine and biology.

11:40am **PB+BI+PS-TuM12 Non-thermal Plasmas in Biomedical Applications– Beyond the Long Lived Species**, ***Kristian Wende***, *J. Volzke*, INP Greifswald, Germany, *J-W. Lackmann*, Ruhr University Bochum, Germany, *H. Jablonowski*, *S. Bekeschus*, INP Greifswald, Germany, *K. Stapelmann*, Ruhr-University Bochum, Germany, *S. Hasse*, INP Greifswald, Germany, *P.J. Bruggeman*, University of Minnesota, *K.D. Weltmann*, INP Greifswald, Germany

Non-thermal plasmas have reached evidence level 2 regarding acceleration of wound healing and in certain aspects of cancer treatment, with a growing community of physicians successfully using it (plasma medicine). Key players in such biomedical applications are reactive oxygen or nitrogen species (ROS/RNS), which are deposited in either tissue (in vivo) or liquid (in vitro) and subsequently influence cellular redox signaling. A huge variety of plasma sources for potential application has been developed and comparing these sources in respect of safety and efficacy remains challenging but desirable.

One aspect can be the identification and quantification of the sources ROS/RNS deposition in liquids. However, due to the short lifetime of many ROS/RNS and limited specificity of available probes their detection is demanding. To meet this challenge, we applied a variety of analytical techniques including high-resolution mass spectrometry of small molecules (cysteine, tyrosine), ion chromatography (RNS detection), electron paramagnetic resonance spectroscopy (O, O_3, $^1O_2$, O_2^-, OH), and colorimetric assays to infer on dominant active species. Two argon plasma jets (MHz jet kinpen, RF jet) and a helium based RF jet (COST jet) were investigated. In addition, cell biology experiments allowed a first estimation of the biological impact of plasma treated small molecules.

A large number of covalent modifications have been detected and in part identified. The majority of changes to the chemical structure of cysteine was found in the vicinity of the thiol group, while in tyrosine the aromatic ring was targeted. The resulting products also occur in physiological situations in vivo, allowing to conclude that the covalent modification of small organic molecules is part of the mechanism of direct plasma-cell interaction. Predominantly short-lived oxygen species were found to be of relevance regarding the chemical and biological impact of plasma, challenging the popular concept of remote treatment (e.g. plasma treated buffers).

12:00pm **PB+BI+PS-TuM13 Effects of Oxygen or Water in Plasma Jet Environment and Feed Gas on DNA Damage**, ***Ek Adhikari***, *V. Samara*, *S. Ptasinska*, University of Notre Dame

Atmospheric pressure plasma jet (APPJ) sources have been explored for applications in industry and medicine. Since environmental conditions such as room temperature and humidity fluctuate, two identical APPJ sources operating at various places and time might perform differently. An APPJ operating in a controlled environment may be able to overcome that issue. Moreover, the interaction of plasma components (e.g., ions, electrons, UV light) with the air in the atmosphere generates the reactive oxygen species (ROS) and reactive nitrogen species (RNS) in the plasma jet [1]. These reactive species can be controlled by adjusting a fraction of oxygen and water vapor in the plasma jet environment and the feed gas. To create a controlled environment for a plasma source, a helium APPJ source was operated in a cylindrical glass chamber with an ambient pressure and filled with pure nitrogen gas along with a fraction of oxygen and water vapor. This APPJ source was used to induce damage in aqueous DNA. The fraction of different types of damaged DNA such as single strand breaks (SSBs) and double strand breaks (DSBs), which were induced due to plasma irradiation, and undamaged DNA were quantified by using agarose gel electrophoresis. We observed that a moderate amount of oxygen and water vapor in the environment, as well as in the feed gas, increases the level of DNA damage.

1. K. Arjunan, V. Sharma, and S. Ptasinska, Int. J. Mol. Sci. **16**, 2971 (2015).

Plasma Science and Technology Division
Room: 23 - Session PS-TuM

Advanced FEOL/Gate Etching

Moderators: Kazunori Koga, Kyushu University, Japan, Erwine Pargon, CNRS-LTM, Université Grenoble Alpes, France

8:00am **PS-TuM1 Highly Selective Silicon Dry Chemical Etch Technique for 7nm FinFET Technology and Beyond**, *Z. Bi*, ***Thamarai Devarajan***, *L. Young*, *B. Miao*, *S. Devries*, *N. Loubet*, *C. Yeung*, *J. Zhang*, *A. Greene*, *H. Zhou*, *M. Wang*, *J. Strane*, IBM Semiconductor Technology Research, *Y. Yao*, IBM, *D. Canaperi*, *C. Surisetty*, IBM Semiconductor Technology Research

With transistor scaling in 7nm technology and beyond, fin spike removal and dummy gate silicon pull are considered to be among the most challenging hurdles in FinFET process development. In this paper, we present a plasma free dry chemical etch technique utilizing NF_3 and H_2 for selective etching of single crystal and polycrystalline silicon at various FinFET device process steps. It was demonstrated that this technique could completely remove poly silicon in vertically high aspect ratio (AR>5) nanosheet FinFET gates with larger process window (overetch budget ~200%), lower gate leakage current and much higher device yield, compared to the technique used in previous generations. Proper surface preparation, queue time control, and etch byproduct removal strategies are discussed. The residue-free etch and etch by-product sublimation mechanisms are also investigated by High Resolution Electron Microscopy (HREM) and Fourier Transform Infrared Spectroscopy (FTIR) surface analysis.

8:20am **PS-TuM2 Anisotropic and Selective Isotropic Etching of Si / SiGe Multilayers in Surface Wave Plasmas**, ***Nick Joy***, *S.A. Voronin*, *P. Biolsi*, TEL Technology Center, America, LLC, *A. Ranjan*, Tokyo Electron Miyagi Limited, Japan

As the feature size of planar devices reaches some fundamental limitations, the continuing drive to increase device density has led to new 3D designs such as fin FETs, nanowire, and vertical FET designs. These innovations bring their own set of challenges for etch applications. While planar devices relied more on anisotropic etching, 3D devices require more isotropic etch capabilities with high selectivity between different materials. For example, one strategy to form nanowire channels is to use multilayered Si/SiGe films that are etched vertically with an anisotropic method to define the width of the wire, and then etched laterally with a selective process that leaves isolated nanowires and allows for deposition of wrap-around gates. Such processes may require either Si selective or SiGe selective isotropic etch capabilities. These abilities have been demonstrated with a RLSA™ plasma etch chamber. Having spatially separated plasma generation and plasma processing regions, RLSA™ etchers benefit from a very low electron temperature (Te~1eV) and low self-bias voltage (i.e. low ion energy) radical-rich discharge. These conditions allow both isotropic and anisotropic selective etching of different materials.

Whether the process is selective to SiGe or Si depends on the chemistry. Generally, it is easier to etch SiGe selective to Si using fluorocarbon plasmas.

The dependency of SiGe recess profiles on pressure, power, and non-fluorinated gas addition show trends that are essentially non-selective to highly SiGe (30% Ge) selective using CF4 based processes. Si selective processes are more difficult to achieve and are sensitive to specific process parameters. However, it is possible to reverse selectivity from Si:SiGe < 1 to Si:SiGe > 1 using SF6 based processes. While the etch mechanism is due to fluorine radicals in both cases, Si:SiGe < 1 may be the result of either lower bond energy of Si-Ge compared to Si-Si, or band gap narrowing with Ge addition[1]. For Si:SiGe > 1, the etch rate of SiGe is inhibited with SF6 gas under the right process conditions, which may be due to preferential deposition of an involatile sulfur blocking layer [2]. This work demonstrates the range of selectivity and isotropic etch capabilities between Si and SiGe using RLSA™.

[1] S. Borel, V. Caubet, J. Bildea, A. Cherif, C. Arvet, C. Vizioz, J.M.Hartmann, G.

Rabillé and T. Billona. ECS Transactions, 3 (7) 627-642 (2006)

[2] G. S. Oehrlein, T. D. Bestwick, P. L. Jones, M. A. Jaso, and J. L. Lindstrorn. J. Electrochem. Soc. 138, 1443 (1991).

8:40am **PS-TuM3 Control of Anisotropic Simultaneous SiGe-Si Etching for Dual Channel Fin Applications**, ***Yohei Ishii***, *M. Walker, R. Scott-McCabe, A. Yu*, Hitachi High Technologies America, Inc., *K. Okuma*, Hitachi High-Technologies Corp., Japan, *K. Maeda, J. Sebastian, J. Manos*, Hitachi High Technologies America, Inc.

As a result of miniaturization by the semiconductor industry to follow the pace of Moore's law, new design approaches to manufacturing have been introduced. Logic device structures have transitioned from traditional planar designs to three dimensional Fin-type Field Effect Transistors (FinFET). This structure change has achieved improved device characteristics such as higher drive currents and lower transistor leakage. To further enhance FinFET electrical performance, a potential approach is the use of high mobility channel materials such as silicon germanium.

In current fabrication schemes, achieving vertical fin profiles and controlling RIE lag are typical issues associated with the fin etch process. However, with the use of silicon in n-FETs and silicon germanium in p-FETs, new etching challenges such as material-dependent etching rate differences have emerged. During the fin etching process, the silicon and silicon germanium must now be etched simultaneously. Silicon germanium etching characteristics have been studied and the results indicate that, with conventional halogen chemistries, the etch rate of silicon germanium is greater than silicon [1]. Should future technology nodes adopt silicon-germanium as a high mobility channel material, etching processes must consider how to control these material-dependent phenomena.

In this presentation, we will introduce an etching process which can be used for dual channel SiGe/Si fin etching. The result shows that the etched amount difference between silicon germanium and silicon can be controlled from a positive value (silicon germanium etching rate is greater than silicon etching rate) to a negative value. Surface analyses were also utilized to further understand the process and the mechanism. Details will be discussed in this presentation.

[1] G.S. Oehrlein, Y. Zhang, G. M. W. Kroesen, E. de Fresart, and T. D. Bestwick, Appl. Phys. Lett. **58**, 2252 (1991)

9:00am **PS-TuM4 Etch Rate and Profile Tailoring of Si and SiO_2 through Laser-Stimulated Thermal Desorption**, ***Jason Peck***, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

In this work, laser exposure was coupled with plasma etch processes for local etch rate enhancement (and under some conditions, etch activation). Materials were tested which are most-frequently used in semiconductor devices – namely Si, SiO_2, and Cu. A 100 Hz, 7 ns pulse width Q-switched Nd:YAG laser was applied at its 1064, 532, and 266 nm modes. Using the 532 nm line on Si (40 mJ/cm^2/pulse) with a radiofrequency inductively-coupled plasma (RF-ICP) source placed upstream, laser etch enhancement effect was 4 Å /s in 50:4 sccm Ar/SF_6, and 3 Å /s etch enhancement at 50:8:2 sccm Ar/C_4F_8/O_2. With no O_2 flow in a 50:8 sccm Ar/C_4F_8 chemistry in an RF capacitively-coupled plasma (RF-CCP) source with a measured self-bias of -140 V, etch activation was seen at 0.62± 0.07 W/cm^2 (6.2± 0.7 mJ/cm^2), with etch rates linearly increasing with laser intensity. The 266 nm line saw etch activation at roughly the same intensity, though etch rate scaling with laser intensity was roughly 6 times higher than 532 nm, corresponding to the drastically-larger absorption depth of 266 nm in Si. No etch enhancement was produced in either chemistry for SiO_2 due to its transparency across the UV-VIS-NIR spectrum, even at 266 nm. CF_x polymer thinning was observed on both Si and SiO_2 at 266 nm but only on Si at 532 nm, indicating a thermally-driven desorption mechanism which relies on heating the material beneath.

It was shown that continuous wave (CW) laser sources of 405, 455, and 520 nm were unable to produce etch enhancement even up to intensities of 200 W/cm^2, demonstrating the necessity of rapid heating of the Q-switched Nd:YAG source (~10s of MW/cm^2 over 7 ns) to temporarily but drastically increase wafer surface temperature. COMSOL simulations showed that a Si surface over the duration of a 532 nm laser pulse would increase temperature by 2.7° C per mJ/cm^2 – a reliably linear rate, even at high intensity. Testing of highly-doped Si wafers revealed a substantial increase in etch enhancement – 10^{19} and 10^{21} cm^{-3} P-doped wafers showed 1.7× and 3.7× higher etch rates over intrinsic Si, respectively. The increased absorption coefficient in these doped wafers confirmed that the etch enhancement mechanism was due to desorption of etch products through thermal heating, rather than through photolytic bond breaking.

Finally, etch tests of 100 nm full-pitch, 100 nm deep trenches showed the ability to tailor etch profile based on wafer orientation. Polarization parallel to the trench line enhanced etching at the top of the features, while perpendicular to the trench line increased trench bottom etch rate.

9:20am **PS-TuM5 Prediction and Control of Fluctuation of Etching Properties by Simulation Technology**, ***Nobuyuki Kuboi***, *M. Fukasawa, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan **INVITED**

Fluctuations of etching properties such as the etched profile and damage distribution can affect the performance of advanced CMOS devices, making the prediction and control of these properties vital for mass production. However, the fluctuations mechanisms are not perfectly understood because of equipment limitations in the plasma monitoring systems used in mass production. Therefore, as a predictive technology, a plasma etching simulation was developed that considers the physical and chemical aspects of the plasma and the etched surface.

We modeled CH_xF_y plasma for SiN etching with a CCP system, taking into account the interaction between the bulk region and the chamber wall surface, and simulated the hydrogen (H) density distribution and H Balmer line emission (virtual OES) [1][2]. From comparisons with experimental OES, the reaction probabilities of H with varying chamber wall conditions (Si, SiO_2, polymer) were derived as 0.5, 0.06, and 0.1, respectively. Using these values, the incident H radical flux was calculated, and found to correlate with the SiN etch rate. This signifies that flux fluctuation is important for controlling the SiN etch rate.

To predict the etched profile and damage distribution for SiN, SiO_2, and Si etching, we developed a new simulation technique using an extended 3D voxel model. This included a Slab model [3] that divides the surface region into several thin slabs and time-dependently solved the surface reactions of its reactive and deposition layers, as well as the depth. We demonstrated SiN sidewall (SW) etching for MOSFET and bulk FinFET with CH_xF_y plasma, successfully describing the etching properties. In addition, a local damage distribution can be seen around the SW edge and in the Si fin, which is difficult to find by experimental analysis. Furthermore, our simulation found that a large amount of Si damage in the Si substrate is caused during SiO_2/Si contact hole etching despite the high SiO_2/Si selectivity (>20) [4], which also exhibits time-dependence. Also, fluctuations of the CD and the Si recess during Si gate etching by HBr/O_2 plasma are greatly affected by the byproduct ($SiBr_x$), exhibiting a dependence on the factor $(R_G+R_S)S$ that includes the wafer (R_G) and chip (R_S) open area ratios, and pattern solid angle (S) [5].

These simulation technologies give us useful knowledge for optimizing the chamber wall condition, plasma etching process, and pattern design for advanced CMOS devices.

[1] Kuboi *et al*., JJAP **49**, (2010) 08JD01.

[2] Fukasawa *et al*., JJAP **48**, (2009) 08HC01.

[3] Kuboi *et al*., JVST A **33**, (2015) 061308.

[4] Nakamura *et al*., JVST A **25**, (2007) 1062.

[5] Kuboi *et al*., JVST A **31**, (2013) 061304.

11:20am **PS-TuM11 Underlayer Impact on Line Width Roughness in Extreme Ultraviolet Lithography and Etch**, ***Indira Seshadri***, *A. DeSilva, Y. Mignot, W. Xu, L. Meli, J. Guo, S. Sieg, J.C. Arnold, N. Felix*, IBM Research Division

Extreme ultraviolet (EUV) lithography enables single expose patterning of fine-pitch features, eliminating the need for complex multiple patterning schemes. However, reduction of line width/line edge roughness (LER/LWR) to match multiple patterning is a fundamental challenge with EUV. Typical EUV patterning stacks consist of resist, hardmask and planarizing organic layer, and reduction of both the post-lithography resist LWR and the post hardmask etch LWR are key to achieving final feature targets. With EUV eliminating the requirement for reflectivity control, hardmask materials may be chosen based on high etch selectivity to resists, stack aspect ratio reduction and low defectivity (eg. Si-containing films). However, recent work[1,2] has shown that hardmask choice can significantly impact fundamental aspects of the lithography that are strongly correlated to LER/LWR, such as dose, process window and EUV secondary electron capture through interactions at

the resist-hardmask interface. Here, we demonstrate the impact of different classes of hardmask materials on LWR in fine pitch metal line features, post litho and post etch. With three classes of hardmasks – Organic spin-on films, inorganic deposited Si-based films, and metal containing films, we first evaluate post lithography LWR with low and high sensitivity resists and dipole and quadrupole illumination shapes. We then characterize LWR after under layer open with optimal etch chemistries to reach target line/space sizes. With frequency analysis of LWR^3, we present fundamental mechanisms that explain the LWR trends arising from resist-illumination-hardmask interaction and etch based LWR smoothing for each class. Our results provide a key knob to aid hardmask selection to meet LWR targets for future nodes

1. A. DeSilva, I. Seshadri, A. Arceo, K. Petrillo, L. Meli, B. Mendoza, Y. Yao, M. Belyansky, S. Halle, N. Felix, "Study of Alternate hardmasks for extreme ultraviolet patterning", J. Vac. Sci. Technol. B 36 (6), 2016.

2. D. De Simone, Y. Vesters,A. Shehzad, G. Vandenberghe, P. Foubert, C. Beral, D. Van den Heuvel M. Mao, F. Lazzarino, "Exploring the readiness of EUV photo materials for patterning advanced technology nodes," Proc. SPIE 10143 (2017).

3. R. Bonam, C. Liu, M. Breton, S. Sieg, I. Seshadri, N. Saulnier, J. Shearer, R. Muthinti, R. Patlolla, H. Huang," Comprehensive analysis of line-edge and line-width roughness for EUV lithography", Proc. SPIE 10143 (2017).

11:40am **PS-TuM12 Patterning Challenges and Perspective Solutions for 5nm and Beyond**, ***Ying Zhang***, Applied Materials, Inc. **INVITED**

Patterning has imposed new challenges and opportunities to Etch, Film metrology. In a variety of multiple patterning schemes, such as Multiple Litho + Etch (LELE…), or Self-Aligned Multiple Patterning (SAxP), Edge Replacement Error (EPE) is approaching the limit, ~¼ of pitch, which will limit the continuing of pitch shrink [1]. The recent development of EUV technology and manufacturability will help to realize much needed complementary lithography technology [2]. The challenges of reducing EPE (< e.g., ~ ¼ pitch), pitch walking, and CD/CDU/LER/LWR controllability in <0.5 nm (3s) regime have shifted from Lithography to Films, Etch and Metrology. Continuous improvements of current plasma etch and film technologies are facing challenges to carry out the tasks of multiple patterning for the industry to extend to 5nm. Can process fine tuning based on current plasma etch and film tool technologies accomplish the precision requirement of fabricating sub-20nm pitch patterning? Atomic Layer Deposition (ALD) technology has already played a key in self-aligned multiple patterning. Further exploring on ALD and gapfill technology to provide more films with conformal and gapfill capabilities are required to enable some highly challenging patterning schemes. Conceptually, Atomic Layer Etching (ALE) should be able to help, e.g., CD control, etch selectivity, etc. But the key question is how to realize true ALE. In this talk, some of the new developments, key challenges, and perspective solutions on processes, process integrations, and plasma etching and film systems for will be reviewed and discussed.

[1] Richard Schenker, Intel, SPIE 2016, Feb, 2016, San Jose, USA

[2] Yan Borodovsky, Intel, Leti Innovation Days, June 26th 2013, Grenoble, France

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+EM+MN+PS+SS-TuA

Nano-Photonics, Plasmonics and Mechanics
Moderators: Joshua Ballard, Zyvex Labs, Christian Zorman, Case Western Reserve University

2:20pm **NS+EM+MN+PS+SS-TuA1 Nonlinear Interactions of Coupled MEMS Cantilevers**, ***Christopher Wallin***, National Institute of Standards and Technology, Center for Nanoscale Science and Technology, *R. De Alba, D.A. Westly,* NIST/CNST, *S. Grutzik,* Sandia National Laboratories, *A.T. Zehnder, R.H. Rand,* Cornell University, *V.A. Aksyuk,* NIST/CNST, *S. Krylov,* Tel Aviv University, Israel, *B.R. Ilic,* NIST/CNST

Micro- and nano-electromechanical systems (M/NEMS) offer tremendous opportunities for technological advancement in mechanical resonator applications including mass, force and energy sensing, microwave amplification, optomechanics, and energy harvesting. These M/NEMS resonators have many favorable qualities including high mechanical quality factors and compatibility with integrated circuit architectures. More specifically, nonlinear, coupled M/NEMS resonating cantilever arrays have been shown to possess complex system dynamics such as intrinsically localized modes, wave propagation, and sensitivity to defects. The collective behavior of these nonlinear interacting cantilever arrays is remarkably sensitive to the slightest perturbation which makes them an excellent candidate for ultra-sensitive sensors. Moreover, custom device responses can be achieved by tuning the electrostatic fringing field coupling, altering the mechanical coupling via the device's overhang, or by introducing precisely engineered structural imperfections into the arrays. With our work, we have found that the cantilever arrays exhibit distinct propagation bands, abrupt transitions between standing wave patterns, and synchronization.

Various device geometries including interdigitated arrays, opposing element arrays, and di-element arrays were constructed using both silicon and silicon nitride as device layers. The arrays generally consisted of 100 cantilevers or more which limited boundary effects in the devices. Gold electrodes were patterned on top of the cantilevers for parametric electrical actuation and for fringing field electrostatic coupling between adjacent cantilevers. Mechanical coupling in the arrays was achieved through the large overhangs produced during the device release. The amplitude envelope of the out of plane motion of the cantilevers was captured using a CMOS camera using a frame rate of 30 s^{-1}. The devices were driven electrically and using a piezoelectric transducer under ambient and vacuum conditions. Large, nonlinear vibrational amplitudes were observed in the arrays along with hysteresis. The cantilever arrays exhibited unique standing wave patterns which were sensitive to defects and external loading. Since the dynamics of M/NEMS coupled cantilevers are highly sensitive to local changes in their environment, we envision the practical implementation of coupled arrays for ultra-sensitive chemical, biological, and force sensors in the future.

2:40pm **NS+EM+MN+PS+SS-TuA2 Silicon Carbonitride Nanoresonator Arrays for Proteomic Analysis**, *W. Zheng,* University of Alberta, Canada, *R. Du,* University of Alberta and The National Institute for Nanotechnology, *Y. Cao,* University of Alberta and The National Institute for Nanotechnology, Canada, *M.A. Mohammad, S.K. Dew,* University of Alberta, Canada, *M.T. McDermott,* University of Alberta and The National Institute for Nanotechnology, ***Stephane Evoy***, University of Alberta, Canada

Analysis of biological molecules is vital in many fundamental problems of molecular biology. ELISA is a widely employed array-based technique for the parallel analysis of biological analystes. This technique however requires fluorescent tagging, which may disrupt the biochemical properties being investigated. Other platforms such as quartz crystal microbalance (QCM) and surface plasmon resonance sensors (SPR) offer alternatives for the analysis of molecular mixtures. However, these platforms are not readily scalable towards large arrays. Resonant mechanical sensors operate by monitoring shifts of resonance frequencies associated to the binding. Such approach enables the frequency modulation of the output, improving the stability/noise-immunity of the reading. In addition, the adsorption sensitivity per unit area of resonators scales favourably as their dimensions are reduced, offering a compelling path for the development large arrays with exquisite mass-sensitivities.

Suspended silicon resonators as narrow as 45 nm were initially reported by Carr, Evoy et al.[1] The brittle properties of this material however limited the yield of these structures to less than 25 %, precluding their use in large arrays. We have recently reinvented the overall approach employed in NEMS fabrication. This new approach combines surface and bulk machining techniques for the release of the device, as opposed to the widely-accepted sacrificial layer approach. We are now routinely fabricating ultra-large arrays of SiCN nanostring resonators as narrow as 8 nm and a yield approaching 100%. These are the narrowest devices produced by any machining method. Each device offers a detection threshold as small as 200 Da. These arrays have successfully been employed for the detection and analysis of protein mixtures. Diazonium modification was developed onto the SiCN surfaces and validated by X-ray photoelectron spectroscopy. Similarly modified nanostrings were then covalently functionalized with anti-rabbit IgG as molecular probe. Specific enumeration of rabbit IgG was successfully performed through observation of downshifts of resonant frequencies. The specificity of this enumeration was confirmed through proper negative control experiments. Helium ion microscopy further verified the successful functionalization of nanostrings.

[1]D. W. Carr, S. Evoy, L. Sekaric, H. G. Craighead, J. M. Parpia, App. Phys. Lett. 75, 920 (1999).

3:00pm **NS+EM+MN+PS+SS-TuA3 Cavity Optomechanical Coupling in Chip-Scale Plasmonic and Photonic Transducers for Nanoscale Measurements and Optical Signal Control**, ***Vladimir A. Aksyuk***, *S. An*, NIST Center for Nanoscale Science and Technology, *B. Dennis*, Rutgers University and NIST CNST, *T. Michels, B.J. Roxworthy, J. Zou*, NIST Center for Nanoscale Science and Technology **INVITED**

Devices controlling light via mechanical motion are ubiquitous, from a simple camera's zoom lens to arrays of moving mirrors correcting for atmospheric distortions in telescopes and digitally projecting movies on the cinema screens. The same optomechanical coupling provides one of the best known techniques for measuring mechanical motion, covering length scales form atomic force microscopy to kilometer scale LIGO interferometers to the red shift measurements over billions of light years. We study optomechanical coupling in micro and nanoscale systems that combine electromechanics with photonics and plasmonics, and apply such chip based optomechanical transducers to solve nanoscale measurement problems. In one example, integrated cavity-optomechanical sensing breaks the common trade-off between sensitivity and bandwidth in atomic force microscopy, allowing extremely low noise motion readout of very fast, nanoscale/picogram mechanical probes. Reducing the probe size not only increases the transduction bandwidth, but also reduces drag and therefore the fundamental thermodynamic force noise when operating in air. Even though the cantilever crossection is much smaller than the optical wavelength, the near-filed coupled high quality factor photonic cavity makes our motion readout exquisitely sensitive. As a second example, I will discuss nanomechanical plasmonic systems, where extreme confinement of the gap plasmon optical modes leads to some of the largest optomechanical coupling coefficients ever observed. I will present electro-mechanical gap plasmon phase modulators and nanomechanically tunable deep subwavelength gap plasmon resonators with potential applications for motion metrology, novel nanoscale sensing and signal transduction and arbitrary wavefront control via nanoelectromechanically tunable optical metasurfaces.

4:20pm **NS+EM+MN+PS+SS-TuA7 An Active Plasmomechanical System for Optical Modulation and Mechanical Lasing**, ***Brian Roxworthy***, *V.A. Aksyuk*, NIST

Plasmonic structures can couple electromagnetic radiation into volumes much smaller than the limits imposed by diffraction. This strong confinement of light transforms these static metallic nanostructures into sensitive bio-chemical sensors, near-field probes for imaging, nanoscale light sources, and effective optical tweezers [1-4]. Advancing the plasmonics paradigm to include active devices, whose resonant properties can be dynamically tuned *via* various electrical, mechanical, or thermal inputs, has great potential to advance nanoscale optical sensing and transduction and for building functional metamaterial devices [5,6].

We present a tunable plasmomechanical system that couples the localized gap plasmon (LGP) resonances of individual subwavelength structures to mechanical, electrical, and thermal modes. By engineering extremely strong optomechanical coupling of the LGPs, we achieve broad tuning of the localized resonances at megahertz frequencies using small voltages < 5 V, producing ≈ 40 % amplitude in the far field and > π phase shift of the re-radiated light. We furthermore show selective, sub-diffraction optical transduction of nanomechanical motion with < 10 fm $Hz^{-1/2}$ sensitivity. Coupling of LGPs to thermal modes results in strong thermomechanical backaction capable of driving regenerative mechanical oscillations of cantilever devices – mechanical lasing – using an isolated, subwavelength plasmonic element. Our platform opens the door to smart metamaterials having programmed responses across physical domains, tunable metasurfaces and optical components, and studying optically-powered nonlinear nanomechanics.

[1] J. Anker *et al.*, Nat. Mater. 7, 442–453 (2008).

[2] D. K. Gramotnev and S. I. Bozhevolnyi, Nat. Photon., 83–91 (2010)

[3] Y-J. Lu *et al.*, Science 337, 450–453 (2012)

[4] B. J. Roxworthy *et al.*, Nano Lett. 12, 794–801 (2012)

[5] N. Zheludev and E. Plum, Nat. Nanotech. 11, 16–22 (2016).

[6] B. J. Roxworthy and V. A. Aksyuk, Nat. Commun. 7, 13746 (2016).

4:40pm **NS+EM+MN+PS+SS-TuA8 Plasmon-enhanced Photo-catalysis Using Collapsible Nano-fingers**, ***Yunxiang Wang***, *B. Song, W. Wu, S. Cronin*, University of Southern California

1. Introduction

Photocatalytic decomposition plays an important role in the treatment of pollutants. It utilizes light radiation to decompose contaminants into non-toxic substances. While TiO_2 is one of the most widely used photocatalysts, visible light can hardly be used to drive TiO_2 due to the short wavelength cutoff of TiO_2. Plasmon-enhanced photo-catalysis can extend the wavelength range due to higher order effects. However, previously reported work has limited efficiency, because the hot spots were not optimized and the TiO_2 located outside the hottest part of the hotspots. Here, we invented a technology to fabricate collapsible nano-fingers to achieve large-area high density optimized hotspots with TiO_2 film located at the hottest part of the hotspots. We demonstrated highest photo-catalysis efficiency that we are aware of.

2. Device fabrication

First, pillar arrays were patterned on the top two layers using UV-curable nanoimprint lithography (NIL) and reactive ion etch (RIE), as shown in Fig. 1(a) (b) (c). Au film was deposited on the sample followed by lift-off process to form gold nanoparticle arrays with diameter of 50 nm and pitch of 200 nm on the bottom layer, as shown in Fig. 1(d) (e). After nano-fingers were fabricated using RIE, 2 nm TiO2 film was deposited on the sample using atomic layer deposition (ALD), as shown in Fig. 1(f) (g). After the arrays were exposed to ethanol solutions and air-dried, the fingers closed together in groups of two or four. The scanning electron microscopic (SEM) image of the collapsed nano-fingers is shown in Fig. 2.

3. Results and Discussion

The photocatalytic activities were tested using methyl orange (MO) photodegradation as the model reaction. The decay in absorbance of the solution was monitored by Varian Cary 50 UV–Vis spectrophotometer after 8 h exposure to green laser (532 nm, 3 W) irradiation. MO solution and sample were added into a standard quartz cuvette sealed with a sealing film.

The absorption spectra taken before and after irradiating are used to quantify the photocatalytic decomposition rate, as shown in Fig. 3. As a control experiment, we firstly performed experiment under same illumination condition with a silicon wafer coated with 2nm TiO_2 film, no MO photodecomposition was observed even after 12 h irradiation. For the monomers, the absorption of the MO solution is observed to drop by 4.9% after 8 h illumination. However, with collapsed sample, a 30% reduction in the MO absorbance is observed. This over 6-fold enhancement demonstrates a stronger plasmonic enhancement after nano-fingers being collapsed, which means this novel structure is a great platform to study plasmonic enhancement.

5:40pm **NS+EM+MN+PS+SS-TuA11 Ultra-High Resolution Photonics-based Thermometry**, ***Nikolai Klimov***, *T. Herman, K.O. Douglass, M.J. Chojnacky, Z. Ahmed*, National Institute of Standards and Technology

Temperature measurements play a crucial role in various aspects of modern technology ranging from medicine and manufacturing process control, to environmental and oil-and-gas industry. Among various temperature measurement solutions, resistance-based thermometry is a time-tested method of disseminating temperature standards [1]. Although industrial resistance thermometers can routinely measure temperatures with uncertainties of 10 mK, their performance is sensitive to multiple environmental variables such as mechanical shock, thermal stress and humidity. Drift of sensor resistance over time necessitates expensive, time-consuming recalibrations using ultra-sensitive reference thermometers. These fundamental limitations of resistance thermometry, as well as the desire to reduce sensor ownership cost have ignited a substantial interest in the development of alternative temperature measurement solutions such as photonics-based temperature sensors. A wide variety of innovative photonic sensors have been proposed recently including functionalized dyes [2], hydrogels [3], fiber optics-based sensors [4], and silicon micro- and nanophotonic devices [5,6]. These innovative temperature sensors have the potential to leverage advances in frequency metrology to provide cost-effective measurement solutions. Here we present the results of our efforts in developing novel on-chip integrated silicon photonic temperature sensors with nanoscale footprint and ultra-high resolution as an alternative solution to legacy-based resistance thermometers. These sensors are Fabry-Perrot cavity type silicon photonic devices that are based on photonic crystal nanobeam cavity (PhCC), whose high-Q resonant frequency mode is highly sensitive to even ultra-small temperature variations. In this talk we describe nanofabrication, fiber coupling and packaging of these thermometers, as well as their performance. We will present a direct comparison of our photonic thermometers to Standard Platinum Resistance Thermometers, the best in class resistance temperature sensors used to disseminate the International Temperature Scale of 1990. The preliminary results indicate that our PhCC nanothermometers are capable of detecting changes of temperature as small as 10 μK and can achieve measurement capabilities that are on-par or even better than the state-of-the-art resistance thermometry.

[1] Strouse, NIST Spec. Publ. 250, 81 (2008).

[2] Donner et al., Nano Lett. 12, 2107 (2012).

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[4] Kersey et al., IEEE Photonics Technol. Lett. 4, 1183 (1992).

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6:00pm **NS+EM+MN+PS+SS-TuA12 Size-Controlled Synthesis of Gold Nanostars and their Excellent SERS and Fluorescence Quenching Properties**, ***Waqqar Ahmed***, *H.I. Khan, M.U. Khalid*, COMSATS Institute of Information Technology Islamabad, Pakistan

Noble metal nanoparticles have attracted great attention recently owing to their fascinating optical properties. They work as nanoscopic antennas by amplifying the incident and scattered electromagnetic beam. The incident electromagnetic radiation can excite the surface plasmons of nanoparticles, leading to the confinement of electromagnetic energy around the nanoparticles. This makes the metallic nanoparticles an excellent candidate for the surface enhanced Raman scattering (SERS) applications. Anisotorpic nanoparticles such as nanostars are much superior for SERS applications over their spherical counterparts owing to the special surface morphology.

We have developed a facile method for the synthesis of gold nanostars with tunable sizes ranging from 50nm to about 1μm. To the best of our knowledge, this is the widest size range reported for gold nanostars. More importantly, we have observed that these nanostars are excellent for SERS based detection owing to their large enhancement factors and efficient fluorescence quenching properties. Fluorescence is known to interfere with and overshadow the SERS signal, thus affecting the trace detection capabilities of SERS. Therefore, usually off resonance excitation lasers must be used for SERS studies of fluorophores, which limits the universal applicability of the SERS technique. We believe that non-compact surfactant coating of nanostars in our case give the target fluorophores access to nanostar's surface, thus enabling the quenching of fluorescence through Förster resonance energy transfer (FRET). The absence of fluorescence background markedly enhances the appearance of Raman peaks. We were able to achieve a limit of detection of 10pM using an excitation laser source in resonance with the electronic excitation of the target fluoropore. This makes gold nanostars universal substrates for SERS based trace detection.

Plasma Science and Technology Division
Room: Ballroom B - Session PS+SS-TuA

The Science of Plasmas and Surfaces: Commemorating the Career of Harold Winters (ALL INVITED SESSION)

Moderators: Sumit Agarwal, Colorado School of Mines, Selma Mededovic, Clarkson University

2:20pm **PS+SS-TuA1 History and Legacy of the Coburn and Winters Paper**, ***R.Mohan Sankaran***, Case Western Reserve University, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

The Coburn and Winters paper[1] is a hallmark contribution in the field of plasma processing. The study revealed very simply and cleverly the role of a plasma in reactive ion etching. When a silicon (Si) surface was exposed to an argon (Ar) ion beam alone or xenon difluoride (XeF_2) alone, the etch rate was found to be negligible. This showed that physical sputtering and chemical etching in the former and latter cases, respectively, could not effectively etch Si. In stark contrast, combining the Ar ion beam and XeF_2 resulted in a significantly higher etch rate, underscoring the synergistic mechanism of fluorine radicals reacting with the Si surface and Ar ions bombarding and kicking them off to ultimately remove Si atoms. The legacy of these experiments is not only the technological impact it has had on applications of plasma processes to semiconductor manufacturing, but, more broadly speaking, the foundation it has laid for plasma science by demonstrating how

a complex system can be unraveled to yield simple correlations. This is reflected here every year at AVS where the etching sessions continue to be the largest of all the sessions in the Plasma Science and Technology Division. In this introductory talk to the session commemorating Harold Winters, a history of the Coburns and Winters experiment and its impact on plasma science and technology will be presented.

1. J. W. Coburn and H. F. Winters, *J. Appl. Phys.***50**, 3189 (1979).

2:40pm **PS+SS-TuA2 The Reaction of Fluorine Atoms with Silicon: Controversies 38 Years in the Making**, ***Vincent M. Donnelly***, University of Houston

Chemical etching of silicon by fluorine atoms in the absence of ion bombardment is reviewed. Controversies on the identity of etching products and reaction probabilities are discussed. Attempts are made to explain the apparent presence of SiF_2 as a primary product in many studies, dating back to 1980, but not in others, including those of Harold Winters from as early as 1979. Reported estimates of reaction probabilities (here defined as the probability of removing a Si atom from the substrate per incident F atom) vary by a factor of 2000. When these values, with some corrections and normalizations applied, are plotted as a function of F atom flux, most of them fall on a "universal curve" that reveals a large (~30-fold) decrease in the reaction probability with increasing F flux, from 0.03 at a F flux $10^{12}cm^{-2}s^{-1}$ to 0.001 at a flux of 10^{20} $cm^{-2}s^{-1}$. These values were extracted from beam experiments with F atoms generated from cracking of F_2, including those by Harold Winters, from isotropic etching in plasma experiments (both in-plasma and downstream) with F_2, $CF_4/10\%O_2$, and NF_3 feed gases, as well as from molecular dynamics simulations. Reaction coefficients derived from chemical etching rates in SF_6 plasmas do not follow this trend, however, suggesting a large enhancement in the F reaction probability (~20 to 100-fold at F fluxes of 10^{18}-$10^{19}cm^{-2}s^{-1}$), due to the presence of sulfur.

3:00pm **PS+SS-TuA3 The Long Quest to Understand Etch Mechanisms and Surface Science: The Legacy of Harold Winters and its Impact on Semiconductor Industry**, ***Sebastian Engelmann***, *N.C.M. Fuller*, IBM Research Division, T.J. Watson Research Center

From the beginning of its days in semiconductor industry until now, Harold Winters work has very big impact to plasma processes and surface science. Starting with his landmark papers in the 1970's and 1980's, much scientific work was inspired by his publications. At IBM itself and industry-wide, many projects were impacted by his work. We will present our view on some of these topics as well as the lasting technological impact that Harold's work had and it inspired.

3:20pm **PS+SS-TuA4 Surface Science Aspects of (Plasma) ALD reactions**, *V. Vandalon, M.C.M. van de Sanden*, ***Erwin Kessels***, Eindhoven University of Technology, The Netherlands

The profound contributions of Harald Winters and John Coburn to the field of plasma etching have inspired us at the Eindhoven University of Technology to study the surface-science aspects of plasma deposition. The latter has been an overarching theme within our research in the last two decades. It started with investigations of the growth mechanism of amorphous carbon and silicon films prepared by plasma-enhanced chemical vapor deposition (PECVD) and it resulted even in beam-experiment-type studies using advanced real-time diagnostic probes in a dedicated high vacuum reactor [1]. The interest in understanding the surface reactions during film growth was also the motivation to step into the field of atomic layer deposition (ALD). ALD film growth is truly ruled by surface chemistry and, inspired by work of others, we recognized that the ALD field could greatly benefit from plasma-assisted processes [2]. Like in other cases of (plasma-based) film growth, a detailed understanding of the surface-science aspects is key to take advantage of all opportunities the method provides. This has been the driver for many experimental studies of the film growth by thermal and plasma ALD using a wide variety of gas phase and surface diagnostics [3]. It has also been the trigger to set up nonlinear optical studies of the surface processes during ALD, culminating in advanced broadband sum-frequency generation (SFG) studies [4]. In this contribution, the historical perspective of our research will be sketched and some recent highlights will be presented.

[1] See for example, J.J.H. Gielis *et al*., Phys. Rev. B 77, 205329 (2008).

[2] See the review paper by H.B. Profijt *et al*., J. Vac. Sci. Technol. A. 29, 050801 (2011).

[3] See for example, Heil *et al*., Appl. Phys. Lett. 89, 131505 (2006) and Langereis *et al*., Appl. Phys. Lett. 92, 231904 (2008).

[4] See for example V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. 108, 011607 (2016).

4:20pm **PS+SS-TuA7 Harold Winters and Plasma-Surface Interactions**, ***David Graves***, University of California at Berkeley

My trajectory in studying plasma-surface interactions was profoundly affected first by reading the papers of Harold Winters, then by talking and working with him. My co-workers and I read and re-read Harold's papers (often co-authored with John Coburn) and the insights we gained from this work had a huge impact on what we chose to investigate and how we interpreted our results. In particular, our early studies of plasma-surface interactions using molecular dynamics simulations were almost completely motivated and guided by his work. Later, I had the extraordinary good fortune to welcome Harold into my laboratory for several years as a visiting scholar. His presence (and that of John Coburn and Dave Fraser) enlightened, instructed and inspired my entire group. I will summarize the impact of Harold's scientific work, his gracious and generous personality and his innate enthusiasm for science on me and my research group.

4:40pm **PS+SS-TuA8 Illuminating the Black Box: Plasma-Surface Interactions at the Atomic Scale**, ***Jane Chang***, UCLA

This talk pays tributes to Harold Winters's seminal contributions in the field of plasma etching of silicon-based materials and metals. Inspired by one of the earliest papers of Harold Winters, where he presented a framework for understanding plasma etching by treating the plasma as a "pseudo-black-box" to provide a semi-quantitative understanding of plasma etching effects such as loading, this talk presents a generalized methodology, combining thermodynamic assessment and kinetic verification of surface reactions, to further illuminate the black box in an effort to tailor plasma-surface interactions for a wide range of materials. This talk does not attempt to review all of Harold Winters's work but focus on his work in metal etch and how that foundational knowledge helps guide the fundamental research in these areas to further advancements in tailoring the plasma-surface interactions to achieve desirable etch efficacy and selectivity of metals at the atomic scale.

5:00pm **PS+SS-TuA9 Controlling Low Temperature Plasma Surface Interactions for Atomic Layer Etching of Electronic Materials And Atmospheric Pressure Plasma-Treatments of Model Polymers and Biomolecules**, ***Gottlieb S. Oehrlein***, University of Maryland, College Park

Harold Winters's pioneering work on the scientific understanding of plasma-surface interactions, in particular as applied to low temperature plasma-based etching of materials, much of it done in collaboration with John Coburn, [1] has become textbook material. As a colleague at IBM Research I had the opportunity to learn from Harold by discussing with him ideas on rate limiting factors in etching reactions, in particular the role of surface reaction layers and the role of ion bombardment. These topics were of great interest to him as a possible explanation of ion-neutral synergy and also of the doping effect of silicon etching. In this talk I will discuss the relationship of Harold's work to topics in my own research, in particular to recent work performed by members of my group. These include atomic layer etching of SiO_2 and other materials[2] and interaction of the effluent of atmospheric pressure plasma sources with polymers and biomolecules.[3]

[1] H.F. Winters and J.W. Coburn, "Surface science aspects of etching reactions," Surf. Sci. Rep. 14, 161 (1992)

[2] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, "Fluorocarbon assisted atomic layer etching of SiO_2 using cyclic Ar/ C_4F_8 plasma", J. Vac. Sci. Technol. A **32**, 020603 (2014).

[3] E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, and G. S. Oehrlein, "On the Interaction of Cold Atmospheric Pressure Plasma with Surfaces of Bio-molecules and Model Polymers", Plasma Chemistry and Plasma Processing **36**, 121 (2016); P. Luan, A. J. Knoll, H. Wang, V. S. S. K. Kondeti, P. J. Bruggeman, and G. S. Oehrlein, "Model polymer etching and surface modification by a time modulated RF plasma jet: role of atomic oxygen and water vapor," Journal of Physics D-Applied Physics **50**, 03LT02 (2017).

* I gratefully acknowledge the contributions and collaboration of D. Metzler, Kang-Yi Lin, C. Li, S. Engelmann, R. Bruce, E. Joseph, E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, V. S. S. K. Kondeti, P. J. Bruggeman and D. Graves to some of the topics in this talk. Additionally, funding from National Science Foundation (CBET-1134273, PHY-1004256, PHY-1415353), US Department of Energy (DE-SC0001939) and Semiconductor Research Corporation (No. 2017-NM-2726) is thankfully acknowledged.

5:20pm **PS+SS-TuA10 H-induced Defect Kinetics in a-Si:H: Obtaining Kinetic Parameters from Temperature-Dependent Data**, *F.J.J. Peeters*, DIFFER, Netherlands, *J. Zheng*, Peking University, China, *I.G.M. Aarts*, ASML, *A.C.R. Pipino*, ONR, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands, ***Richard van de Sanden***, DIFFER, Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) has been applied to study the defect evolution in an a-Si:H thin film subjected to a calibrated directed beam of atomic H at different substrate temperatures (80 to 200 °C) . To this end a 42 ± 2 nm a-Si:H film was grown on the Total

Internal Reflection (TIR) surface of a folded miniature optical resonator by Hot-Wire Chemical Vapor Deposition (HW-CVD). A fully reversible defect creation process is observed, with a non-linear dependence on H flux, with a time resolution of 33 ms and a relative sensitivity of 10^{-7}. Through the use of polarizing optics the CRDS signal was split into *s*- and *p*-polarized components, which, combined with *E*-field calculations, provides depth sensitivity. Extensive kinetic modeling of the observed process is used to determine rate constants for the hydrogen-material interactions and defect formation in a-Si:H, as well as revealing a high diffusion coefficient for atomic H on the order of 10^{-11} cm^2s^{-1}. A novel reaction pathway is proposed whereby H inserted into weak Si-Si bonds recombines with mobile H, resulting in a limited penetration depth for atomic H from the gas-phase on the order of 15 nm. The defect evolution kinetics can be modeled based on a quasi-steady-state approximation of H atoms, which assumes that the H density in the film reaches a quasi-steady-state very rapidly and exhibits little change with time. This approximation significantly simplifies the kinetic model, accurately predicts the initial absorption change behavior and allows quantitative evaluation of the kinetic parameters of the microscopic processes and the corresponding activation energies.

5:40pm **PS+SS-TuA11 Translating Fundamental Science to Technology Development in Plasma Assisted Materials Processing: Contributions by Harold Winters and Their Impact on Modeling**, ***Mark Kushner***, *C.M. Huard, S.J. Lanham, S. Huang, P. Tian*, University of Michigan

A hallmark of the contributions of Harold Winters to the advancement of plasma materials processing is beginning with fundamental processes, and building upon this foundational knowledge towards technology development. His contributions to our understanding of ion assisted chemical sputtering, adsorption, desorption, chemisorption, conductance in features, stopping distances, mixing layers and electron impact dissociation cross sections are examples of producing foundational knowledge which enabled the work of colleagues in the field. This enabling aspect of his work is nowhere more true than for modeling and simulation, as first principles models begin with these foundational principles. In this talk, key foundational contributions by Harold Winters in plasma-surface interactions and electron impact processes will be reviewed from the perspective of enabling first principles modeling. Examples will be discussed from reactor and feature scale modeling of conductor and dielectric plasma etching, with emphasis on aspect ratio dependent etching and atomic layer etching.

Work was supported by National Science Foundation, Department of Energy Office of Fusion Energy Science, Lam Research and Samsung Electronics.

6:00pm **PS+SS-TuA12 Extending the Legacy of Harold Winters: Probing the Energetics and Plasma-Surface Interface of Halogenated Plasmas**, ***Ellen Fisher***, Colorado State University

In the arena of halocarbon plasma chemistry, Harold Winters and co-workers performed pioneering work by extensively exploring plasma-assisted etching of semiconductor materials using a range of halogenated systems. For example, Coburn and Winters explored the role of energetic ions in plasma-assisted etching in silicon-fluorine systems, studying the dynamic interplay between physical and chemical sputtering. This work has inspired several decades of work on halogenated plasma systems, including further elucidation of the role of ions and other energetic species within plasmas. In this work, energy partitioning for molecules formed from fluorinated plasma systems has been measured using laser-induced fluorescence, optical emission and broadband absorption spectroscopies. Focusing on two fluorinated species, SiF in SiF_4 plasmas and CF_x in C_xF_y fluorocarbon plasmas, we find that small molecules in these systems exhibit extremely high electronic excited state vibrational temperatures, T_V, relative to rotational temperatures, T_R. This suggests that vibrational modes are preferentially excited over other degrees of freedom. Using the imaging of radicals interacting with surfaces (IRIS) technique, surface scattering coefficients measured for each radical show a strong correlation with the associated T_V, with little dependence upon $T_R$or translational temperatures. This presentation will focus on plasma deposition and etching systems where understanding the relationship between the gas-phase and the resulting surface properties allows for deeper insight into creating advanced functional materials for a range of applications. Specific examples will include fluorocarbon film formation as well as production and modification of multidimensional materials.

Plasma Science and Technology Division
Room: Central Hall - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Particle Kinetic Simulation of Low-temperature Low-pressure HiPIMS Plasma, *N.T. Lauer*, ***Natale Ianno***, University of Nebraska-Lincoln

Leveraging the advantages of high impulse magnetron sputtering (HiPIMS) requires knowledge of the temporal evolution characteristics and transport properties of the target material from the cathode to the substrate. These are difficult characteristics to measure directly. Determining the desired process parameters required for specific results by experiment, such as pulse voltage, duty cycle, pressure, magnetic field strength and profile, electrode separation, substrate biasing, and target current density, is time consuming and expensive involving multiple experiments combined with months of characterizing depositions. Also, this approach must be repeated for each target material and gas mixture used. This makes the ability to model and predict plasma properties and deposition or etching results due to external driving parameters via computer simulation attractive.

A *1d3v* particle-in-cell (PIC) *local density adjustment* Monte-Carlo-Collision (LDA-MCC) model has been applied to model the specifics of sputtering using HiPIMS. Physics of the plasma-target interaction and diagnostics were incorporated into the model resulting in the ability to better understand the target species evolution at the cathode and subsequent transport to the substrate. The LDA-MCC was used regarding specific collision types to support transient particle volume density gradients and population inversions in the plasma associated with HiPIMS. Temporal evolution of species energy distribution functions (EDFs), volume densities, and populations at various locations within the plasma are characterized. Simulation predictions are compared with a variety of different experimental results in the literature supporting the validity of the model. These results will support future enhancements to the model to explore substrate bias effects on the process of target ion transport, tailoring energy distributions of deposited ions at the anode, investigating the utility of synchronized pulsed substrate biasing, and their effects on deposition characteristics.

PS-TuP2 QDB: the Quantemol Database of Plasma Processes, *C. Hill, S. Rahimi, D.B. Brown,* ***Anna Dzarasova****, J.R. Hamilton, S. Zand-Lashani,* Quantemol LTD, UK, *J. Tennyson*, University College London, UK

QDB (https://quantemoldb.com)[1] is a database of plasma reactions and chemistries which is being expanded to include surface interactions and processes occurring at interfaces. This database aims to become a basis for computational model development for plasma-assisted processes. Such processes have become more and more popular, and increasingly allow better control and achieve high precision[2]. A way to reduce development risks in plasma chamber design and process optimisation is modelling the plasma kinetics and better understanding plasma-surface interactions. This, in turn, requires an understanding of processes using atomic-scale physics and where scaling becomes non-linear.

The QDB web software provides a platform for users to download, upload, compare and validate data, and exposes an Application Programming Interface (API) for its automated retrieval in a range of formats suitable for use in modelling software. The software was used to deposit industrial plasma chemistries developed within Powerbase project to be accessed via the API using specifically. Experimental validation was provided by industrial partners of Powerbase project. The library of chemistries and examples and datasets has been further developed with both experimental and theoretical sources by Quantemol staff and by our community of users.

In this presentation we will describe recent Powerbase developments in QDB, with a focus on the increased provision of data relating to the interaction of particles with surfaces. This has required the expansion of the QDB data model to include a characterization of the surface (substrate) composition and structure as well as the description of the behaviour of individual adsorbed species (desorption energy, diffusion energy, etc.)

It is hoped that the database and its associated online web application software and API will prove useful to the AVS community, particularly in commercial and academic research areas related to modelling plasma-enhanced processes.

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Acknowledgment: this project has received funding from the Electronic Component Systems for European Leadership Joint Undertaking under grant agreement No 662133. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Austria, Belgium, Germany, Italy, Netherlands, Norway, Slovakia, Spain, United Kingdom.

PS-TuP3 Self-neutralized Ion Beam by Pulsed Plasma with Synchronous Afterglow Bias, ***Ya-Ming Chen***, *R. Sawadichai, V.M. Donnelly, D.J. Economou*, University of Houston

Precise control of the ion flux and ion energy distribution (IED) is crucial for advanced plasma processes that require high selectivity and minimum substrate damage. To neutralize the space charge of the ion beam extracted from a plasma, hot filaments, emitting electrons thermionically, are strategically placed on the downstream side of the extraction grid. Charge neutralization prevents spreading of the ion beam by Coulomb collisions among the ions. This work reports our observation that a self-neutralized ion beam can be obtained when the beam is extracted in the afterglow of a pulsed plasma. Specifically, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias on an electrode in contact with the plasma (so-called boundary electrode) during a specified time window in the afterglow of a pulsed plasma. The ion beam flux in the pulsed plasma case was much higher than that in a continuous wave plasma under comparable conditions. Retarding Field Energy Analyzer measurements of the ion flux and IED with varying control parameters (including plasma pulsing frequency, and the time delay in the afterglow before a DC bias was applied on the boundary electrode) were performed to provide a plausible explanation of the system behavior.

Work supported by NSF.

PS-TuP4 Gold Nanoparticle Catalyst for Plasma Nitridation of Thin Films, ***Takeshi Kitajima***, *Y. Kariya, T. Nakano*, National Defense Academy of Japan, Japan

Gold nanoparticles show a catalytic features which depends on its size.

We tried to apply the catalytic property of the gold nanoparticles to a thin film processing under a plasma exposure. The catalysis enhanced process has a possibility of a low damage plasma processing that eliminate ion bombardments and charge trapping.

The example of the process is Si nitridation using low pressure nitrogen plasma.

Gold nanoparticles are self-assembled on a SiO_2/Si(100) sample surface after the deposition of gold using an e-beam evaporator in an ultra high vacuum environment. After a 2 min. of gold deposition, hemispherical nanoparticles with the average width of 13.6 nm is formed. The number density of the nanoparticles is 6.0 e11 cm^{-2} and most of the surface area is covered with gold.

Inductive coupled plasma of 50 MHz excitation and 30 mTorr of nitrogen pressure is exposed to the sample with gold nanoparticles on the surface. After the plasma exposure, the surface morphology of the sample shows increased uniformity of the gold nanoparticle size. The nitridation degree of Si is examined with XPS.

Due to the N1s XPS signal ratio to the other component like Si2p, O1s, Au4f and C1s, nitrogen composition on the surface is evaluated.

The nitrogen composition of the samples with and without gold nanoparticles is 6.2 and 5.0 % after the plasma exposure of 15 s.

Even though the direct ion exposure to the SiO_2 layer is inhibited by gold nanoparticles, Si sample is nitridated at similar rates with the aid of the catalytic effect of gold nanoparticles. The catalytic effect of the gold nanoparticles in this process is presumed to be the atomic transport of nitrogen atoms physisorbed on the nanoparticle surface to the underlined SiO_2 interface and subsequent chemical reaction to form SiON.

The process with nanoparticle catalyst is expected to perform on various atomic layer synthesis like graphene functionalization and so on.

PS-TuP5 Development of Microwave Resonant Probes for Measurement of Plasma Density, ***Bo-Jr Chen***, *Y.C. Wu, J.S. Chiou, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Low temperature non-equilibrium plasma discharges are of great interests for applications ranging from micro/nano fabrication to bio/medical treatments. The density of the plasma discharge governs the basic characteristics of these plasma processes. In this study, microwave based diagnostics are developed for plasma density measurement or even process monitoring. The first device is a compact plasma absorption probe (C-PAP), a simple electric dipole like probe where the tip is formed by the center conductor of a coaxial semi-rigid cable, which is enclosed by a dielectric tube. The probe operated under the "resonant" mode, i.e., detecting the resonance frequency when the probing microwave and the nature frequency of the structure from by the probe and the surrounding plasma medium. The probe is designed by employing three

dimensional electromagnetic numerical simulation analysis (HFSS, ANSYS Corp) where the plasma is treated as a dielectric with dielectric functions determined by plasma density, microwave frequency and collision frequency of electrons. The effects of plasma sheath and presheath are also investigated in the simulation analysis. The simulation results are used to calibrate the results from experimental measurements. The second resonant type probe under development is a spiral probe (SP) where the structure is a shorted microstrip transmission line. The first resonance of this structure occurs at the frequency where the transmission line becoming a half wavelength resonant structure. The spiral probe is designed for mounting on a chamber wall to minimize perturbation to the plasma discharges. Experimental and simulation results of the C-PAP, as well as the initial simulation analysis of the SP will be presented.

Acknowledgement

Work supported by the Ministry of Science and Technology, ROC (Taiwan).

PS-TuP7 Molecular Dynamics Simulation of Ni Self-sputtering and Modeling of Interatomic Potential Functions, ***Nicolas Mauchamp***, *M. Isobe, S. Hamaguchi*, Osaka University, Japan

Plasma etching techniques have been widely used to manufacture semiconductor devices. Typical device scales of silicon (Si)-based field effect transistors (FET) are now approaching atomic scales. For the further development of plasma etching techniques to fabricate such small devices, a good understanding of plasma-surface interactions is indispensable. For example, during a plasma etching process with energetic ion bombardment, damages may be induced and lead to the formation of non-functional regions inside the created device structures. Therefore plasma-induced damages have to be avoided as much as possible.

In the production of magnetoresistive random-access memories (MRAM), stacks of thin layers of magnetic metals and insulators are deposited and etched to form magnetic tunnel junction (MTJ) cells. In typical manufacturing processes of MTJ cells, ion milling with energetic Ar+ ions are used. However, to further miniaturize MTJ cells and increase the MRAM integration, one would need less damaging and more selective etching processes for magnetic materials and insulators. The ultimate goal of this study is to establish reactive ion etching (RIE) processes for MTJ cells and we approach this goal by examining etching characteristics of magnetic materials with various reactive ions theoretically, using molecular dynamics (MD) simulations and first-principle quantum mechanical (QM) simulations. In this study, we take nickel (Ni) as a sample magnetic material.

In classical MD simulations, the interatomic potential models must be selected from the existing models or created based on QM simulation. It has been found that, with most existing interatomic potential models for Ni, the physical sputtering yields of Ni obtained from ion beam experiments for high ion incident energies cannot be reproduced by MD simulation. Therefore, in this study, we have focused on self-sputtering of Ni and examined the dependence of the self-sputtering yield on the interatomic potential functions. Since the Ni self-sputtering yield at a high ion incident energy sensitively depend on the short-range repulsive atomic interaction, we have determined the short-range interatomic functions based on experimentally observed Ni self-sputtering yields. It has been found that the newly adjusted interatomic potential model for Ni, which is based on the embedded atom model (EAM), can reproduce experimentally obtained Ni self-sputtering yields over a wide range of ion incident energy. Using the newly created interatomic potential model, we have also determined the dependence of the Ni self-sputtering yield on the ion incident angle.

PS-TuP8 Atomic Layer Etching of Silicon Dioxide Using Alternating C_4F_8 and Energetic Ar^+ Plasma Beams, *S. Kaler, Q. Lou, V.M. Donnelly,* ***Demetre Economou***, University of Houston

Atomic layer etching (ALE) of SiO_2 was studied by alternating exposure of a 5 nm-thick SiO_2 film on Si substrate to (1) a plasma beam emanating from a c-C_4F_8 inductively coupled plasma (ICP), to grow a fluorocarbon (FC) film composed mainly of CF_2, and (2) an energetic (130 eV) Ar^+ ion beam extracted from a separate Ar ICP. *In-situ* X-ray photoelectron spectroscopy was used to analyze the chemical composition of the near-surface region, and to quantify the thickness of the FC and SiO_2 films. A very thin (3-6 Å), near self-limiting thickness CF_2-rich FC film was found to deposit on the SiO_2 surface with exposure to continuous or pulsed power C_4F_8 plasma beams, under conditions that generated a large relative flux of CF_2. Following this, a FC film of similar composition grew at ~10 times slower rate. Exposure of the thin film to the Ar^+ beam led to removal of 1.9 Å SiO_2. An estimated yield of 1.3 SiO_2 molecules-per-Ar^+ was found for a single ALE step. The rate of 1.9 Å/cycle persisted over multiple ALE cycles, but a carbon-rich residual film did build up. This film can be removed by a brief exposure to an O_2-containing plasma beam. Support from Lam Research and NSF is gratefully acknowledged.

PS-TuP9 Si, SiO_2, and Si_3N_4 Etching Characteristics of Silicon Halide Ions (SiF_x^+, $SiCl_x^+$, and $SiBr_x^+$), ***Kazuhiro Karahashi***, *T. Ito, H. Li, Y. Muraki,* Osaka University, Japan, *M. Matsukuma,* Tokyo Electron Limited, Japan, *S. Hamaguchi*, Osaka University, Japan

Reactive ion etching (RIE) by halogen-based plasmas is widely used for etching of silicon-based materials such Si, SiO_2, and Si_3N_4 in semiconductor manufacturing processes. As semiconductor devices continue to be miniaturized, a better understanding of basic reactions of etching and/or deposition processes on substrate surfaces has become more important than before for finer controls of device structures in the manufacturing processes. In etching processes of silicon-based materials by halogen-based plasmas, Si atoms desorbed from the surface as etching products may enter the plasma (as ions such as $SiBr_x^+$ or charge neutral radicals such as $SiBr_x$) and return to the surface, forming an additional silicon-based material layer on the substrate as well as hard mask materials (such as SiO_2, and Si_3N_4). Therefore it is important to clarify etching characteristics of silicon-halides ions for Si, SiO2, and Si3N4 substrates for the development of highly controllable etching processes with halogen-based plasmas. Beam experiments of such etching processes offer useful information for a better understanding of interactions of individual species contained in a plasma with the surface. In this study, etching and/or deposition reactions of Si, SiO_2, and Si_3N_4 substrates are examined with the use of a mass-selected ion beam system, which can clarify the roles of silicon (Si^+), halogen (F^+, Cl^+, and Br^+), silicon mono-halide (SiF^+, $SiCl^+$, and $SiBr^+$), and silicon tri-halide (SiF_3^+,$SiCl_3^+$, and $SiBr_3^+$) ions for etching of Si-based materials. Si+ irradiation below 1000eV deposits silicon atoms on Si, SiO_2, and Si_3N_4 surfaces. Similarly, at sufficiently low incident energy, a silicon mono-halide ion beam also deposits silicon on the surface. The etching yield by silicon tri-halide ions is typically larger than three times the etching yield by single-halogen ions. Experimentally obtained etching yields or deposition rates for various combinations of Si-based substrates and incident silicon halides as functions of incident ion energy offer critical information for the further development of highly precise etching processes.

PS-TuP10 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In Situ* Measurements of Local Excitations in Thin Films, ***Eric Gillman***, Naval Research Laboratory, *B.M. Foley, J. Tomko,* University of Virginia, *D.R. Boris, S.C. Hernández,* Naval Research Laboratory, *A. Giri,* University of Virginia, *Tz.B. Petrova, G.M. Petrov,* Naval Research Laboratory, *P.E. Hopkins,* University of Virginia, *S.G. Walton*, Naval Research Laboratory

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physicochemical changes associated plasma-based materials processing. The unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure the electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the excited electrons propagate radially from the point of contact. These results, in conjunction with plasma characterization, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

PS-TuP11 Modeling of a Plasma Discharge in an ICP Plasma Source for a Strip Tool, ***Vladimir Nagorny***, Mattson Technology, Inc., *V.V. Olshansky,* Kharkiv Institute of Physics and Technology, Ukraine, *S. Ma*, Mattson Technology, Inc.

Inductively coupled plasma (ICP) sources have been used in plasma processing for more than two decades, and will be used in a foreseen future. For a photoresist (PR) strip direct plasma interaction with a wafer is undesirable and plasma is used mainly for modification of a gas composition and creating chemically active radicals for processing the wafers. To achieve high ash rates strip tools usually operate at very high flows since a PR strip rate directly relates to the flux of radicals to the surface of the wafer.

Typical fluxes in strip sources are about or exceed 5slm per head and the gas pressure varies in the range of 0.5-5 Torr. At these high gas pressures, electron energy relaxation length for high energy electrons is very short and these electrons can only be in equilibrium with the local effective electric field E_{eff} rather that with other electrons. That strongly affects both the

distribution of energy deposition into plasma, rates of kinetic processes and the field penetration into the plasma volume. A high plasma density, high gas temperature (low gas density N) region is formed near the coil, where reduced electric field E_{eff}/N is high enough to sustain the ICP discharge in a wide range of process gas pressures and flows, while outside of this region E_{eff}/N is low and ionization is negligibly small.

In this presentation we compare results of plasma simulations in ICP strip source from the common model with drift-diffusion approximation for both electrons and ions and Maxwellian EEDF for electrons with similar simulations using a new model, where in the hot region the drift-diffusion approximation is used only for ions. As for electrons, they are considered in balance with the effective electric field, and the drift-diffusion approximation for them is used only outside the hot region.

PS-TuP12 Characterization of Ion Lasers with Paschen Curves, ***Steven Flores***, San Jose State University and Coherent Inc., *C. Fields*, Coherent Inc.

Paschen curves for argon and krypton are obtained by measuring the breakdown voltage of gases in an ion laser plasma tube. The data are taken at various pressures (voltages) with fixed electrode separations. Paschen curves can be used to determine the optimal setting of an ion plasma laser based on minimal breakdown voltage for a given plasma power. The Paschen curves vary with gas type and pressure. The trend lines can also be used to indicate the presence of impurities in the plasma.

PS-TuP13 Plasma Simulation of Capacitively Coupled Plasma for High Aspect Ration Contact Process of Semiconductor, ***Hyowon Bae***, Samsung Electronics Co. Ltd., *J. Kim*, Pusan National University, Republic of Korea, *M. Lin*, Hanyang University, Republic of Korea, *J. Um, S. Han, T. Kang*, Samsung Electronics Co. Ltd., *H.J. Lee*, Pusan National University, Republic of Korea

High aspect ration contact process has been important process to make dynamic random access memory(DRAM) and NAND flash memory with large sotrage and high speed. Plasma etching technology has been studied for few decades, and plasma uniformity or chemistry can be controlled on these days under some condition. However, plasma etching process is still very tough to obtain the result which we wish with high frequency up to 100 MHz and high power over 10kW. Therefore, control of plasma under these condition is required to be sucesseful plasma etching result, which leads to obtain almost same etching result at all area of wafer from center to the edge. It also promises high yield and high profit in the industry. Capacitively coupled plasma(CCP) is most popular method in etching and deposition process. Plasma simulation is performed in this study to obtain the plasma distribution for unifrom etch rate at all area. Under the specific condition, uniform plasma can be shown. Ion enegry distribution, ion flux, and other physics will be explained in this presentation.

PS-TuP14 N_2, O_2, and NF_3 Dissociation in a Low Frequency, High Density Plasma Source, ***Hanyang Li***, *Y. Zhou, V.M. Donnelly*, University of Houston, *K. Wenzel, J. Chiu, J. Lamontagne, X. Chen*, MKS Instruments, Inc.

Most capacitive and inductive plasmas used in deposition and etching tools for semiconductor processing operate at pressures in the sub-Torr regime (typically <200 mTorr) at relative low power densities (~0.01 – 0.1 W/cm^3). Higher pressure, high power density plasma sources offer significant advantages in improved cost of ownership through increased tool throughputs, but have not received as much attention in the academic world. In this poster we present measurements of radical densities and gas dissociation fractions for various mixes of N_2, O_2, and NF_3 feed gases with Ar at 400 sccm total flow rate in a low frequency (400 kHz), high pressure (1-10 Torr), inductively-coupled toroidal remote plasma source from MKS Instruments operating at a power density of 5 – 50 W/cm^3. The radical densities and feed gas dissociation percentages in the plasma were measured by optical emission spectroscopy (OES), combined with Ar actinometry. The dissociation of O_2 drops from 55% to 10% with increasing O_2 percentage, while the dissociation of N_2 rises from 10% to ~100% with increasing N_2 percentage. For NF_3, the dissociation to form F rises with increasing NF_3 percentage from 60% at 1% NF3 and to 100% at 10% NF_3, while about 25% of the nitrogen is present as N_2, independent of NF_3 percentage, with presumably some or nearly all of the remaining nitrogen present as N atoms, which are detected in optical emission. Enhanced or suppressed dissociation as a function of added Ar will compared with changes in discharge current, relative electron density and other plasma parameters.

PS-TuP16 Improvement of Adhesion Strength between Copper and Composite Materials using Plasma Press Method, ***DooSan Kim***, *W.O. Lee, J.W. Park, M.K. Mun, K.S. Kim, K.H. Kim, Y.J. Ji, J.S. Oh, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Adhesion is one of the important issues for the wearable, attachable, and implantable devices. Especially, adhesion strength between hetero interfaces is very important. Various methods such as hot press, UV curing, thermal curing, and hot press after plasma treatment have been investigated to improve adhesion strength between different interfaces. But, for flexible devices, the adhesion strength obtained by these existing methods adhesion appear not enough and a higher adhesion force is required. In this study, in order to improve the adhesion strength between hetero interfaces, a novel plasma press method was introduced, and where, two interfaces are press bonded while plasma is on. The experiment was conducted in order to improve the adhesion strength between prepreg (Prepreg is a polymer substrate contained resin. Prepreg was also used as an insulating layer) and copper foil. These materials are used for the fabrication of multilayer flexible printed circuit board (PCB) substrate. The adhesion measurement was conducted by a peel off test. The plasma press method improved adhesion strength about 75 % compared to the conventional hot press method. The stronger bond for the plasma press is believed to be related to the formation of active carboxyl functional groups and unsaturated dangling bonds on the materials surfaces by the plasma operating during the hot press for bonding.

PS-TuP17 Experimental and Simulation Study on Hydrogen Atom Kinetics in Low-pressure Capacitively Coupled Plasmas, *S. Nunomura, K. Katayama*, ***Isao Yoshida***, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In plasma processing, a hydrogen (H) atom is a key species (a radial) that strongly influences the gas-phase reactions and surface reasons. So, the investigation on H atom reaction kinetics is beneficial for controlling the gas-phase species and the material surface property. Here, we study the H atom generation and loss kinetics in low-pressure capacitively coupled plasmas (CCP).

We performed the H density measurement in CCP in two different configurations of electrodes: direct and remote configurations. In direct configuration, the processing material was exposed into the plasma, whereas in the remote configuration, the processing material was separated from the plasma by the metal mesh to reduce the ion bombardment and charging. The H atom density was quantitatively determined from vacuum ultra violet absorption spectroscopy (VUVAS) [1]. We found that the H atom density was strongly reduced across the mesh electrode in the remote configuration. For example, the H atom density was varied from ~1x10^{10} cm^{-3} in the discharge region to ~1x10^{12} cm^{-3} in the processing region for our mesh geometry of 0.2 mm thickness and 36% aperture ratio [2].

The fluid model simulations for CCP discharges have been performed to study the details of the H atom generation, diffusion and recombination kinetics [2]. The simulation yielded the H atom density of~1.0 x 10^{12} cm^{-3}, which was in good agreement with that measured by VUVAS. The H atoms are generated mainly in the discharge region, via two processes: the electron impact dissociation ($e + H_2 \Rightarrow e + 2H$) and the ion-molecule reaction ($H_2^+ + H_2 \Rightarrow H_3^+ + H$). For the loss of H atoms, it is dominated by the surface recombination on the electrode. In the presentation, more details of experimental and simulation results are presented.

The authors are grateful to Dr. Y. Abe (Tokyo Tech.), Prof. N. Ezumi (U. Tsukuba), and Prof. N. Ohno (Nagoya U.) for valuable discussions. This work was supported in part by New Energy and Industrial Technology Development Organization (NEDO) and JSPS KAKENHI (Grant Number 24540546 and 15K04717)

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PS-TuP18 Effect of Superimposed Multi-frequency on Plasma Characteristics of an Inductively Coupled Plasma Source, ***Kyung Chae Yang***, *H.S. Lee, S.G. Kim, D.I. Sung, M.K. Mun, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

To achieve reduced production cost and improved productivity for nanoscale semiconductor devices, the specifications of dry etchers have become more stringent. One of the important specifications for next generation plasma systems is the extremely high uniformity from center to edge of the substrate. Especially for inductively coupled plasma (ICP) sources, as the power to the ICP sources is increased for increased plasma density, non-uniform power deposition resulting in non-uniformity of the plasma has increased further. Recently, numerous theoretical and experimental studies have been performed to improve the plasma uniformity such as separate dual frequency excitation, very high frequency mixing, etc. However, controllability of a plasma uniformity over a large area substrate still remains as one of the major challenges.

In this study, as one of the methods in controlling the plasma uniformity, superimposed multi-frequency operation on an ICP source has been investigated. On the ICP source, dual frequency power selected from 2~ 40

MHz was applied and, on the substrate, a single frequency was applied, and the effect of power ratio of multi-frequency power on the plasma characteristics including the etch uniformity was investigated for a 300 mm diameter ICP etch system. The variation of multi-frequency power at a same total power changed the electron energy distribution profiles and plasma uniformity. When SiO_2 wafer was etched using Ar/CF_4, an improved etch uniformity by using a multi-frequency operation of the ICP source could be observed.

PS-TuP19 Numerical Simulation of Capacitively Coupled Radio Frequency Plasma Discharges - Effect of Hollow Cathode Structure, ***Hsin-Chang Chang***, *C.Y. Chen, P.S. Luo, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Radio frequency capacitively coupled plasmas (CCPs) are important plasma reactors for applications in a wide range of areas such as thin film deposition and dry etching, etc. The property of the discharge, e.g., plasma density and uniformity, can be tailored or enhanced by integrating the hollow cathode effect. In this study, fluid model numerical simulation is employed to investigate the effect of slots or holes on the grounded electrode, instead of the powered electrode as in conventional hollow cathode enhanced CCPs, on the discharge characteristics. Two different CCP reactors are investigated. The first one is an indirect Ar/H_2 CCP where a grounded mesh is placed between the two electrodes of a conventional CCP. The effect of the side of the holes on the plasma behavior, as well as the dependence of the ratio of ion to neutral radicals fluxes are analyzed. Simulation Results show that, as a result of the grounded mesh/grid that separating the two chambers, the flux of both ionic and reactive neutral species drop significantly, by a factor of ~1/1000 - 1/10000, from the top main chamber to the bottom drift chamber. This, in term, implies that the ion energy flux incident on the grounded bottom electrode should be minimal, and thus damage to the substrate surface due to ion bombardment can be significantly reduced. Moreover, simulation results show that hole size less than sheath thickness is needed for low ion flux toward substrate and low plasma potential in the bottom chamber. The second reactor we investigated is a CCP with a slot on the top grounded electrode while the bottom one is powered by rf voltage. Simulations are carried out for two different feed gases, Ar and CF_4. Results from parametric studies and comparisons of hollow cathode effect between electropositive and electronegative discharges will be presented.

Acknowledgement

Work supported by the Ministry of Science and Technology, ROC (Taiwan).

PS-TuP20 Photocatalytic Effects of Ag-TiO_2 Nanotubes Fabricated by BCP Lithography, *G.Y. Yeom*, ***Dain Sung***, *J.S. Oh, K.C. Yang, D.W. Kim*, Sungkyunkwan University, Republic of Korea

Titanium dioxide (TiO_2) is one of the multipurpose materials used for various functional applications such as solar photocatalysts for degradation of environmental contaminants due to its unique properties. Especially,environmental decontamination by photocatalysis using TiO_2 nanotubes can be more appealing than conventional chemical oxidation methods because of its low costs, nontoxicity, high surface-to-volume ratios, high surface activity, and simple recycling. In addition, noble metal nanoparticles, such as Ag nanoparticles, doped on the surface of TiO_2 nanotubes can increase their photocatalytic activities and can be easily fabricated by a photochemical deposition method under UV light irradiation. Among various methods to fabricate of TiO_2 nanotubes, TiO_2 nanotubes fabricated by using block copolymer (BCP) lithography and reactive ion etching (RIE) can form uniformly aligned nanoscale morphorlogies.

In this study, using the TiO_2 nanotubes fabricated with BCP lithography, TiO_2 atomic layer deposition (ALD), and RIE and Ag nanoparticles precipitated on TiO_2 nanotubes by a photochemical method, the photocatalytic effect of TiO_2 nanotubes with/without Ag nanoparticles was investigated by measuring the concentration change of a methylene blue solution. The photocatalytic effect of TiO_2 nanotubes was higher than flat TiO_2 film because of the increased TiO_2 surface area. Also, Ag nanoparticles attached on the TiO_2 nanotubes further improved the photocatalytic effect by facilitating electron–hole separation and promoting interfacial electron transfer process through the Ag nanoparticles. However, when the amount of Ag nanoparticles on TiO_2 nanotubes are too much, possibly due to the decreased UV penetration to TiO_2 by the increased surface area covered with Ag nanoparticles, the photocatalytic effect was decreased. By precipitating 7~9 nm size Ag nanoparticles for 20 min on 40~50 nm diameter/50~60 nm height TiO_2 nanotubes, the highest photocatalytic effect could be obtained.

PS-TuP21 Prediction of Particle Generation by Machine Learning in Plasma Etching Tools, ***Yoshito Kamaji***, Hitachi High-Technologies Corp., Japan, *M. Sumiya, A. Kagoshima*, Hitachi High-Technologies Corp., *M. Izawa*, Hitachi High-Technologies Corp., Japan

Prognostics techniques, which predict the remaining useful life of the components and monitor the health conditions of process equipment by utilizing data-sets that acquired from the sensors of equipment components, are gaining attention to solve the cost issues in semiconductor manufacturing. [1].

In this study, development of a prognostics system to predict the health conditions that deviated over time in microwave plasma etching tools was investigated. The selection of the right analytical engines for getting effective results has been a major issue that impedes deployment of prognostics techniques. Several machine learning algorithms including PCA-based T-squared /square prediction error (SPE) [2], self-organizing map (SOM) - minimum quantization error (MQE) [3], auto-associative kernel regression (AAKR) [4] were evaluated to predict particle generation for the etching of metal layers such as work function metals (WFMs). The benchmarking results indicated that AAKR and PCA-T squared most effectively captured particle generation and showed better monitoring performance compared with other algorithms. In addition, process parameters that affect the particle generation were clarified by calculating contribution values for each process parameter. Details will be discussed in this presentation.

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PS-TuP22 Investigation of Wear-Resistance Enhancement of Plasma-functionalized Carbon-nanotube Composite Polyurethane Film, ***Daisuke Ogawa***, *H. Uchida, K. Nakamura*, Chubu University, Japan

We have investigated possible causes of mechanical enhancement for a composite polyurethane (PU) film with plasma-treated carbon nanotubes (CNTs). Wear-resistance is a main topic here in terms of mechanical property. Our preliminary result showed that wear-resistance was improved by means of making a CNT-composite PU film, in particular, in the case when the CNTs treated with the plasma, which is made with gas mixture of nitrogen and carbon dioxide, was utilized. In order to enhance such a mechanical property of PU, we considered the following two possibilities; the wear-resistance increased due to 1) a uniform spatial distribution of CNTs in a PU film and/or 2) the fact that plasma-treated CNTs gives additional wear-resistance from chemical aspects, possibly from functional groups on CNTs. In fact, it is known that isocyanate (NCO) group is sometimes utilized in order to enhance their mechanical property of PU. First, we observed our CNT composite PU films with optical microscopy. The observation showed that the spatial distribution of CNTs in a composite PU film was not really enhanced due to plasma treatment by comparing with other CNT composite PU film. The circumstance indicates that the plasma-treated CNTs enhances the wear-resistance of PU film possibly from chemical aspect. However, we know that this is still in the range of our speculation. Therefore, we have recently focused on making a direct identification of NCO groups on the plasma-treated CNTs. In this presentation, we will show our recent results whether or not our plasma-treated CNTs actually have NCO groups on CNTs, in particular more NCO groups on the CNTs treated with nitrogen and carbon dioxides than those with other plasma treatment. Here, we utilized acridine yellow (AY, $C_{15}H_{15}N_3$), which is a good indicator of NCO groups by using photoluminescence (PL). AY solution (2mg/L AY in tetrahydrofuran, THF, C_4H_8O) was added the solvent dispersing CNTs to attach AY and NCO groups. And then, the PL emission was observed. Our result showed that PL emission was observed from the samples relating with the CNTs exposed to the plasma made with nitrogen/carbon dioxide and only with carbon dioxide plasma. In fact, we did not expect to observe PL emission from the CNTs treated with carbon dioxide plasma because the lack of nitrogen species in this gas composition. However, the residue of air gas might have provided the species, and showing the emission. In this presentation, we will show more recent results and analysis of identification of NCO groups on CNTs.

PS-TuP23 Dynamics of Power-Modulated Chlorine Plasmas, ***Tianyu Ma***, *T. List, P. Arora, Y. Zhou, V.M. Donnelly*, University of Houston, *S. Nam*, Samsung Electronics, Republic of Korea

Studies of power-modulated chlorine inductively-coupled plasmas will be presented. Power at 13.56 MHz applied to the plasma was modulated between a high power and low power state. This allows optical emission and actinometry with trace added Ar to be carried out during the entire period, unlike traditional pulsed plasmas where no power is input during the “low power” state. Optical emission spectra were recorded over the 200 to 900 nm region where emissions from Cl, Cl_2, SiCl, $SiCl_2$, $SiCl_3$ and Ar occur. The intensity of Cl-to-Ar emission, proportional to Cl number density, was strongly modulated, allowing Cl recombination coefficients to be obtained

from a simple model. Langmuir probe measurements were also recorded. The plasma was found to operate in one of two modes. When power was dropped from high to low, ether 1) the plasma density and optical emission intensities quickly dropped to a lower level that then remained constant, or 2) the density dropped to a very low level, emission ceased for a rather long time until re-ignition occurred. Whether the plasma operates in mode 1 or 2 is sensitive to settings on the matching network and is also a function of pressure and modulation frequency.

Work supported by Samsung Electronics.

PS-TuP25 Investigation of Electromagnetic Effects in Very High Frequency Linear Plasma Source, ***Xiaopu Li***, *K. Bera, J.A. Kenney, S. Rauf, K.S. Collins*, Applied Materials, Inc.

Very high frequency (VHF) capacitively coupled plasmas (CCP) are widely used for materials processing in the semiconductor industry. The spatial distribution of plasma in CCP discharges can be affected by electromagnetic effects. In this study, a VHF linear plasma source is considered, which consists of parallel metal bars enclosed within ceramic insulator tubes. The linear source is immersed inside the discharge volume, which is enclosed by a grounded metal box except for the input and output ports. A full three dimensional electromagnetic plasma model is used to understand the interactions between the external radio-frequency source and the plasma. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species concentrations are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are fully described by the Maxwell equations with the plasma current density updated from the fluid model. The RF source in the model excites a transverse electromagnetic (TEM) wave through the input ports. The CPML absorbing boundary condition is applied at the termination port to avoid electromagnetic wave reflections back into the plasma. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. Ar discharge is studied based on the reaction mechanism similar to the previous study [1]. The plasma density profile is found to be dependent on excitation frequency, pressure and power. The spatial distribution of plasma with in-phase and out-of-phase excitation from the ports is investigated as well.

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PS-TuP26 Modeling of High-Density Magnetically Enhanced Inductive Plasmas Generated by Symmetrical Solenoid Coils, ***Bocong Zheng***, *M. Shrestha, Q.H. Fan*, Michigan State University

A magnetically enhanced inductive plasma source (MEIPS) was proposed to address the limitations of conventional inductively coupled plasma (ICP) sources. The MEIPS combined two solenoid induction coils wound in opposite directions and the grounded ends were positioned on the dielectric window. The capacitive coupling between the plasma and the coils was subsequently minimized. The induction coils created a confined magnetic field within the plasma region, leading to a significant increase in the energy-coupling efficiency. To understand the plasma characteristics under different conditions, the MEIPS discharges were modeled and compared with a conventional planar coil ICP discharge. It was found that the MEIPS could generate a much higher plasma density than the conventional ICP discharge under the same input power. By inserting a ferrite core into the coils, the MEIPS discharge could ignite at ~2 MHz and the plasma density dramatically increased with the increase in the frequency until ~6 MHz. Then the plasma density decreased gradually as the frequency further increased due to the dramatically reduced permeability at high frequencies. Comparing with an air core, the ferrite core led to more stable magnetic field distribution with a higher maximal flux denisty ***B***.

PS-TuP27 Plasma Modeling in the OpenFOAM Framework, *A.K. Verma*, ***Venkattraman Ayyaswamy***, University of California Merced

As emphasized in the 2012 Roadmap for low temperature plasmas (LTP), scientific computing has emerged as an essential tool for the investigation and prediction of the fundamental physical and chemical processes associated with these systems. While several in-house and commercial codes exist, with each having its own advantages and disadvantages, a common framework that can be commonly developed by researchers from all over the world will likely accelerate the impact of computational studies on advances in low-temperature plasma physics and chemistry. In this regard, we present a finite volume computational toolbox to perform high-fidelity simulations of LTP systems. This framework, primarily based on the OpenFOAM solver suite, allows us to enhance our understanding of multiscale plasma phenomenon by performing massively parallel, three-dimensional simulations on unstructured meshes using well-established high performance computing tools that are widely used in the computational fluid dynamics community. In this talk, we will present preliminary results obtained using the OpenFOAM-based solver suite with benchmark three-dimensional simulations of microplasma devices including both dielectric and plasma regions. We will also discuss the future outlook for the solver suite.

PS-TuP29 The Role of Charge Exchange Collisions in Selective Etching of Si, ***Sergey Voronin***, *P. Biolsi*, TEL Technology Center, America, LLC, *A. Ranjan*, Tokyo Electron Miyagi Limited, Japan

Continuous shrinkage of transistors in sub-7nm technological nodes requires new integration and etching challenges. As the direct scaling of the FinFET to 5nm is extremely difficult, the use of a 3D integration scheme is considered to be a prospective way toward the next technological node. In addition to generic process requirements (high anisotropy, minimum CD loading and high selectivity to the mask films), conductor etching in such structures is more complicated due to different positions of the stopping layers. Features with deep etch targets may face underetching, while features with short targeted depths may have severe notching due to excessive positive charge of the stopping layer. Fast neutral beam processing in ion-assisted reactive etching is one of the ways for the induced charge mitigation and to eliminate this unwanted effect.

We report a study of Si etching in an HBr/Ar surface-wave Radial Line Slot Antenna plasma. The ability of RLSA^{TM} plasma etchers to operate in a very wide range of the pressures allows the etch process well above 100mT. Process operation in this high pressure range and large Ar^{+}-Ar charge-exchange cross sections (~$3x10^{15}$ cm^{-2} at 100's eV) result in numerous charge exchange collisions in the plasma sheath, leading to a significant presence of the fast neutrals.

A simple model for the ion and neutral energy distributions in an HBr/Ar plasma discharge has shown a significant input of the neutral ion beam. With the exception of the results for the hydrogen and bromine ions, the calculated fast neutral fluxes for Ar can be up to 70% of the total ion flux with the energies comparable to the ions. Reducing operating pressures below 50mT with increase in the plasma density provides etching mostly caused by ions. This correlates well with the experimental etch profiles suffered from notching and bowing.

PS-TuP30 Development of an Aluminum Nitriding Process using Electrostatic Plasma Mass Spectroscopy and Energy Analysis and In Vacuuo Auger Electron Spectroscopy, ***Christopher Muratore***, m-Nanotech Ltd., University of Dayton, *A. Korenyi-Both*, Tribologix Inc.

Aluminum nitride is a hard, wear resistant surface. Modifying an aluminum alloy surface by diffusion based plasma treatment is one potential approach for increasing the wear resistance of aluminum components, however, a review of the literature and discussion with industrial nitriding operations reveal that there are a number of challenges associated with this task. The primary challenge is initial removal of the native oxide formed spontaneously on aluminum surfaces, and inhibiting its formation during the process, even at high vacuum. Using a novel plasma nitriding process,thick aluminum nitride layer (>1 micron) was produced on 6061-T6 alloy samples. Key steps included removal of the oxide layer and identification of pulse characteristics fpr the applied power to the cathode. These steps were accomplished using unique in situ process diagnostics including Auger electron spectroscopy to identify the time and conditions required to clean the aluminum surface and plasma mass spectrometry and energy analysis to identify the optimum ratio of atomic nitrogen atoms compared to molecular nitrogen ions, as identified in prior works for nitriding of stainless steel. It is observed that maximizing the number of atomic nitrogen ions yields higher nitriding rates for aluminum.

PS-TuP31 A New Transformer Model for Solenoidal ICP Discharge Expandable to Low Density Plasma, ***Jang-Jae Lee***, *S.J. Kim, K.-K. Kim, Y.S. Lee, S.J. You*, Chungnam National University, Republic of Korea

A transformer model is well known as model for the analysis of the physics of inductively coupled plasma source. However, this model can be applied only at high density region where the skin depth is much smaller than the chamber radius. In this study, a transformer model which can be applied even under long skin depth conditions was presented. The expression of fields in the plasma source is derived in a one-dimensional geometry and the circuit components of transformer model as a function of electron density can be obtained by the spatial integrating the fields. Comparing these results with those obtained from Maxwell's equation, we confirmed that the results agree with each other in various conditions.

PS-TuP32 Development of a Novel VI Sensor for RF Power Measurement, ***Kwang-Ki Kim***, *S.J. You*, Chungnam National University, Republic of Korea

VI sensor plays an important role in dynamic impedance matching in RF power systems for various plasma fabrication processes. Therefore, many kinds of VI sensors have been developed for several years. However, these sensors have an issue of VI coupling that a transformer coil only for detecting

current also detects voltage which is for detecting of a voltage sensor. In order to reduce the voltage in the coil, we used a novel double shielding walls that can shield the voltage from the coil effectively. We confirmed a voltage and current ratio in the coil using an electro-magnetic simulation by changing the walls' height, position and gap between the walls then analyzed to find VI coupling minimization condition. We developed highly well VI decoupled sensor that has a phase difference about 1.32 degrees between the voltage and current compare to the other sensor that has the phase difference above 20 degrees in a condition of ideally phase difference zero.

PS-TuP33 Transmission Line Model of Cutoff Probe, ***Si-Jun Kim***, *J.-J. Lee, K.-K. Kim, Y.S. Lee*, Chungnam National University, Republic of Korea, *D.W. Kim*, Korea Institute of Machinery and Materials, Republic of Korea, *J.H. Kim*, Korea Institute of Standards and Science, Republic of Korea, *S.J. You*, Chungnam National University, Republic of Korea

Transmission line(TL) model was applied to cutoff probe(CP), which is a microwave resonance probe for measuring electron density. Application of preceding model(circuit model) for analysis of characteristics of CP was limited

to low electron density regime(< 1010 cm-3). In order to supplement the circuit model we introduced TL model and compared results between TL model and three-dimensional full-wave electromagnetic(3-D FWEM) simulation. Simulation

results of TL model are in good agreement with that of the a 3-D FWEM simulation in both low and high electron density regime. Furthermore the results of TL model are the same with that of circuit model in the low electron density

regime. Therefore by using TL model we can expand the applicable range of cutoff probe up to high electron density regime.

PS-TuP34 Fault Detection in Radio-frequency Plasma Processing using Voltage-current (VI) Probes and Statistical Models, ***Thomas Gilmore***, Impedans Ltd, Ireland

Radio-frequency (RF) voltage-current (VI) probes, mounted between the matching network and plasma reactor, can accurately detect plasma impedance changes at the fundamental and harmonic frequencies. The plasma impedance is very sensitive to any electrical, mechanical and/or geometrical changes that may occur in the reactor. The nonlinear nature of the plasma impedance generates a rich harmonic spectrum, accurate measurement of which can be used to precisely detect faults that affect the electrical, geometrical or mechanical integrity of the plasma process. Examples of such faults include; electrical integrity of the RF connections, misplaced substrates, broken focus rings, leaking valves, plasma confinement issues and parasitic plasma formation.

In this poster, we summarize the results of fault detection studies across several RF processes and across a number of industry sectors. It was found that for certain gross faults, such as plasma not igniting, the fundamental voltage, current, and phase angle are sufficient for detection. However, many fault types are more subtle. For example, a wafer misplaced by less than a millimeter off-centre does not show any significant deviation in the fundamental parameters. Higher order harmonics, on the other hand, can show significant variation. It was found that the exact harmonic properties (voltage, current or phase) that are sensitive to the fault are also process and reactor dependent.

The statistical approach used relies on a preliminary baseline measurement of a faultless process across the full spectrum of parameters detected by the RF VI probe. The analysis runs continuously and a Z-score technique is applied to all parameters. A deviation from the “normal” is considered significant if it exceeds six standard deviations (Six Sigma). Data from live semiconductor wafer production will be presented showing fault detection due to wafer misplacement. Charts of various other faults and their significance in terms of sigma-number will also be presented for other processes. This approach can be used to implement alarms on plasma processing tools when faults are detected, preventing costly product scrappage events.

PS-TuP35 Finding Adequate Global Model of Non-Maxwellian Distribution based on PIC Simulation, ***Young-Seok Lee***, *S.J. Kim, J.-J. Lee, S.J. You*, Chungnam National University, Republic of Korea

The electron energy probability function (EEPF) is usually assumed to be Maxwell distribution for 0-D global model. Meanwhile, it is well-known that the form of EEPF of Ar plasma changes from bi-Maxwellian to Druyvesteyn as the gas pressure increases. Thus, to apply the 0-D global model of Maxwellian distribution to the non-Maxwellian plasma, we weighted up the relative contribution of two distinct electrons with different temperatures. The contributions of cold/hot electrons to the power and particle balance were investigated by comparing the result of the global model considering all combinations of electron temperatures with that of 1-D particle-in-cell Monte Carlo collision (PIC-MCC) simulation and the result of investigations was analyzed physically. Furthermore, predictions consistent with PIC-MCC simulation for variations of the contribution of cold/hot electrons at different pressures and driving currents are presented.

Plasma Science and Technology Division
Room: 22 - Session PS+NS+SS-WeM

Plasma Processing for Nanomaterials & Nanoparticles

Moderators: Hisataka Hayashi, Toshiba, Japan, Kazunori Koga, Kyushu University, Japan

8:00am **PS+NS+SS-WeM1 Plasma Catalysis: a Powerful Blend of the Four States of Matter**, ***Kostya (Ken) Ostrikov***, Queensland University of Technology and CSIRO, Australia **INVITED**

Plasma catalysis is a rapidly emerging multidisciplinary field at the interface of catalysis, nanotechnology, physical chemistry, materials and plasma science. Relevant applications include plasma-assisted catalytic reforming of gas mixtures into fuels, chemicals and synthesis of functional nanomaterials. Plasma-specific effects play a major role in nanoscale catalytic phenomena. The process outcomes are improved when catalysts with nanometer-scale surface features are used along with atmospheric-pressure plasmas (APPs). It is possible that plasmas and catalysts act synergistically.

I will review the APP interactions with the nanometer-size features on the surface of catalyst nanoparticles (NPs). Basic understanding of plasma-catalyst interactions is achieved through nd the effects of these modified surfaces on catalytic reactions. Nanoscale interactions of APPs with the NPs and synergistic effects are related to plasma modifications of catalyst structure and reactivity. The synergistic effects may increase the yield and selectivity of catalytic reactions of importance to chemical and energy resource industries.

The focus is on gas mixtures relevant to natural reforming or hydrogen production by water splitting. The selected nanomaterials catalyze the conversion of the above gas mixtures into higher-value products such as synthetic gas (syngas), hydrogen, fuels, etc. of demand in a variety of industrial applications (e.g., methanol production). The plasmas induce "epigenetic" modifications of catalytic materials and the plasma process parameters are customized to maximize both the conversion rates and the process gas flow, i.e., both the outcome (selectivity) and the productivity (rates) of the gas conversion.

I will discuss the most effective nanoscale plasma-surface interactions. The focus will be on surface modifications (e.g., functionalization, expression of crystal facets, changes in reactivity of near-surface atoms, oxidation or reduction states, etc.) of localized surface areas induced by the nanoscale plasma-surface interactions and chemical reactions. The plasma effects enhance reactivity of the "epigenetically" modified surface areas of the NPs. The expected effects include better adsorption, higher conversion rates of reactant species on the modified surfaces, larger surface areas for reactions, higher catalytic activity through more effective electron transfer, reduced reaction activation barriers, photon- and ion-assisted reactions, new plasma-enabled reaction pathways, etc.

8:40am **PS+NS+SS-WeM3 Vaporization of Nanoparticles in Low Temperature Plasmas**, ***Necip Berker Uner***, *E. Thimsen*, Washington University in St. Louis

Particle nucleation is a major problem that occurs in many thin film processing plasmas. The resultant "killer particles" can create defects upon deposition on the film and they can consequently decrease device functionality. A change of perspective, within the last two decades, the aptness of low temperature plasmas (LTP) for particle nucleation has been successfully exploited to synthesize monodisperse, free standing, spherical and crystalline semiconductor nanocrystals from vapor precursors. These impressive properties of particles synthesized in LTPs stem from particle charging and ion bombardment. When the particle number density is smaller than the ion density, it is proposed that the particles experience unipolar charging. The negative charge acquired by the particles suppresses coagulation and leads to uniform growth. On the other hand, ion bombardment elevates particle temperatures above the surrounding gas temperature and provides crystallinity. By using LTPs, nanocrystals of silicon, germanium, various oxides, sulfides and compound semiconductors of high quality have been produced, whereas production of metal particles were less successful, which indicates incomplete understanding.

In this study, we focus on the interaction between the plasma and metal nanoparticles. In an environment free of vapor precursors, we demonstrate that particle growth in LTPs follows a reversible path. Instead of continuous growth, ion bombardment can lead to extensive vaporization, depending on the plasma density and vapor pressure. By sending in a premade aerosol of bismuth particles through a capacitively coupled radio frequency argon plasma, we observed complete vaporization of the metal at moderate power inputs. Interestingly, at low power inputs, vaporization resulted in significant restructuring of the particle size distribution. Polydispersed size distributions were transformed into monodispersed distributions, with relatively high mass yields reaching 65%. Based on spatial Langmuir probe measurements and detailed aerosol dynamics modelling, we propose that upon exposure to different plasma densities, particles can vaporize and then the resultant vapor can either nucleate into particles or recondense on the remaining clusters, eventually leading to the modification of the size distribution. When particles vaporize completely and the vapor is conserved, the result is the conversion of a polydispersed size distribution into a monodispersed size distribution. This unusual mechanism that involves vaporization at low temperature will be detailed with further experimental observations with different materials. Methods of tuning the final size will be elaborated.

9:00am **PS+NS+SS-WeM4 Nanowires, Trusses and Pillars Produced by Assembly of Plasma Generated Nanoparticles**, ***Ulf Helmersson***, *S. Ekeroth, S. Askari, R. Boyd, N. Brenning*, Linköping University, Sweden

Nanoparticles generated or supplied to a plasma attains a negative potential due to the nature of the plasma. This open up interesting possibilities in synthesis and assembly of the nanoparticles creating structures in the nano- and micro-range. In this work, we use hollow cathode sputtering powered with high-power pulse to ensure close to full ionized of the source material. This promotes rapid growth of the nanoparticles to desired sizes and the negative charge makes it possibility to guide nanoparticles for assembly and collection on desired positions. This is demonstrated by attracting nanoparticles to substrate positions with a positive potential and focusing nanoparticles through a matrix of electrostatic lenses to assemble the nanoparticles into pillars. For ferromagnetic nanoparticles, we also demonstrate generation of nanowires as well as nanowires cross-linked into trusses. Since the iron nanoparticles are generated under relatively pure condition they assemble into wires without oxides in the interfaces. Nanowires and trusses assembled on conducting substrates can potentially be used as low cost large area electrodes.

9:20am **PS+NS+SS-WeM5 Non-Equilibrium Plasmas for Nanoparticle Synthesis: from Semiconductors to Metals**, ***Rebecca Anthony***, Michigan State University **INVITED**

Nonthermal plasmas have been increasingly popular for synthesis of nanocrystals. Generally, these flow-through reactors are radiofrequency (RF) plasmas operated at reduced pressure (2-10 Torr) into which vapor-phase precursors are entrained. The nanocrystals form following dissociation and clustering of the precursor molecules. Among the advantages offered by plasma reactors are low-temperature environment, avoidance of liquid-phase reactants, tunable nanocrystal properties via reactor parameters, and scalability. In addition, the nanocrystals can be collected as powders for post-processing, or directly impacted onto substrates in thin-film form, sidestepping the need for additional steps such as spin- or drop-casting. Combined with the solvent-free, low-temperature, all-gas-phase nature of nonthermal plasma reactors, this opens the door to direct incorporation of nanocrystals into functional layers on arbitrary substrates - without concern about solvent orthogonality or thermal susceptibility.

Here we present our work focusing on exploiting the non-equilibrium of plasma reactors for high-quality nanocrystal growth. First we discuss silicon nanocrystals for optical applications. The properties of these nanocrystals, such as size, crystallinity, and surface, can be altered in-flight using the plasma reactor parameters - and they can be inertially impacted onto a variety of substrates. These nanocrystals exhibit efficient and tunable photoluminescence, and we have deployed them in LEDs, luminescent layers on stretchable substrates, and as sensitizers for pollutant photodegradation. The non-equilibrium environment of the plasma also allows growth of even higher-melting-point nanocrystals, and we will share our work on GaN nanocrystal growth using plasma reactors. These freestanding nanocrystals are size-tunable and have excellent crystal quality despite GaN having a bulk melting temperature of 2500°C. Finally, we will discuss formation of metal nanoparticles in the plasma using an altered-geometry RF plasma with a central consumable ground electrode, working towards expanding the range of optoelectronically functional nanomaterials that can be made using nonthermal plasmas.

11:00am **PS+NS+SS-WeM10 Photochemical Insulator-Metal Transition in Plasma-Synthesized ZnO Nanocrystal Networks**, ***Benjamin Greenberg***, *Z. Robinson, K. Reich*, University of Minnesota, *C. Gorynski*, University of Duisburg-Essen, Germany, *B. Voigt*, University of Minnesota, *G. Nelson*, Creighton University, *L. Francis, B. Shklovskii, E.S. Aydil, U.R. Kortshagen*, University of Minnesota

Nonthermal plasma synthesis has recently emerged as a promising method for producing highly conductive ZnO nanocrystal (NC) networks. The

plasma-synthesized NC surfaces are free of ligands, which enables high interparticle electron mobility. In this work, we produce ZnO NC networks using nonthermal plasma synthesis integrated with supersonic inertial impaction deposition, and we manipulate their electron transport properties with a combination of UV illumination and NC surface modification via atomic layer deposition (ALD). Specifically, we use these treatments to increase the free electron density, n, and the interparticle contact radius, ρ, and thereby induce a transition from variable range hopping to metallic transport. We determine n from the NCs' localized surface plasmon resonance (LSPR) and ρ from the subtle increase in the ZnO volume fraction, and we use Fourier transform IR spectroscopy (FTIR) to ascertain the underlying NC surface photochemistry.

11:20am **PS+NS+SS-WeM11 Elucidating Energetic Trends in Hydrocarbon Plasma Systems for Plasma-Assisted Catalysis**, ***Tara Van Surksum***, *E.R. Fisher*, Colorado State University

Plasma-assisted catalysis (PAC) has been investigated as a promising method for pollution control, specifically for conversion or removal of volatile organic compounds. The utility of PAC is severely limited by an overall lack of understanding of plasma chemistry and the reactions occurring at the plasma-catalyst interface. The present work focuses on investigating fundamental gas-phase chemistry in hydrocarbon inductively-coupled plasma systems to understand energy partitioning in PAC systems for decomposition of volatile organic compounds. We have employed broadband absorption and optical emission spectroscopies to determine rotational and vibrational temperatures (T_R and T_V, respectively) for multiple species (e.g., CH, C_2) in a variety of hydrocarbon-containing plasma systems. For example, in CH_4 plasmas, T_V(CH) ranges from ~3000 to ~5000 K, whereas T_R(CH) generally reaches values ranging from 1000-2000 K. Energy partitioning for the same species has also been assessed when a catalytic material (e.g., flat and nanostructured SnO_2 and TiO_2, micro-structured zeolites) is placed in the plasma. In some cases, the substrate has a measureable effect on the gas-phase chemistry, whereas in others the substrate does not appreciably alter the gas-phase of the plasma. Catalytic material properties were also evaluated via surface analysis tools (e.g., X-ray photoelectron spectroscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy) and will be presented in conjunction with energy partitioning data to further elucidate information on the molecular-level processes occurring at the plasma-catalyst interface. Collectively, these data aim to unravel the complex chemistry of hydrocarbon plasma systems for PAC to achieve a viable method of pollution control.

11:40am **PS+NS+SS-WeM12 Synthesis of Metal Nanoparticle Electrocatalysts for Fuel Cell Applications by Atmospheric-Pressure Plasma Reduction**, ***Joffrey Baneton****, Université Libre de Bruxelles, Belgium, *Y. Busby*, Université de Namur, Belgium, *W. Debouge*, Université Libre de Bruxelles, Belgium, *G. Caldarella*, Université de Liège, Belgium, *J.-J. Pireaux*, Université de Namur, Belgium, *V. Debaille*, Université Libre de Bruxelles, Belgium, *N. Job*, Université de Liège, Belgium, *M.J. Gordon*, University of California at Santa Barbara, *R.M. Sankaran*, Case Western Reserve University, *F. Reniers*, Université Libre de Bruxelles, Belgium

Nanoparticles composed of one or more metals particularly platinum (Pt) are used as electrocatalysts in hydrogen fuel cells for the cathodic reduction of dioxygen [1]. Several challenges remain in their synthesis including controlling their morphological features (e.g. size, shape, etc.), maximizing the amount of Pt exposed while minimizing the overall amount of the expensive metal, and eliminating the presence of organic capping groups or other contaminants that cover the active surface.

Here, different atmospheric plasma devices including a microplasma and a radio-frequency (RF) plasma torch are shown to be capable of producing Pt and Pt-based alloy nanoparticles without any organic capping molecules and minimal chemical additives. The as-synthesized nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) to assess their chemical purity and morphology. We find that when using the microplasma to reduce a Pt precursor in solution, small and non-agglomerated Pt nanoparticles can be directly produced in liquid phase (organic or water based). By controlling the initial amount of the Pt precursor dissolved in solution and the charge injected in the system, the nanoparticle concentration can be tuned [2]. Moreover, this methodology can be applied to bimetallic alloys to reduce the amount of Pt in the electrocatalyst.

In comparison, when using a RF plasma torch, Pt nanoparticles can be produced in the solid phase by plasma reduction of a Pt precursor dispersed on the surface of a carbon support (carbon black, carbon xerogel, carbon nanotubes or graphene) [3]. A mechanism for the plasma reduction of Pt is proposed. It is shown that the size distribution of the particles, their dispersion at the surface, and their quantity in the bulk determined by inductively coupled plasma mass spectrometry (ICP-MS), can be fully controlled by the plasma and preparation parameters.

The Pt nanoparticles synthesized by either method are finally used to fabricate the cathode of a proton exchange membrane fuel cell (PEMFC) using a gas diffusion layer as a substrate. The cell performance, represented by the ratio of the electrochemically active surface area (ECSA) and the catalytic activity, which are comparable to commercial cells, will be discussed in detail.

[1] H.A. Gasteiger et al. *In*: W. Vielstich, A. Lamm and H.A. Gasteiger (eds.), Handbook of Fuel Cells – Fundamentals, Technology and Applications, Wiley, Chichester (UK), **2003**, Vol.3, p. 593.

[2] C. De Vos et al. *J. Phys. D: Appl. Phys.* (**2017**), 50, 105206.

[3] D. Merche et al. *Plasma Process. Polym.* (**2016**), 13, 91–104.

12:00pm **PS+NS+SS-WeM13 Microplasma Spray Deposition of Metal Oxide Nanostructures for Energy Applications**, ***Katherine Mackie***, *M.J. Gordon*, University of California at Santa Barbara

A general, substrate-independent method for plasma deposition of nanostructured, crystalline metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) with remote anode to deliver a highly-directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., CuO, α-Fe_2O_3, and NiO) can be deposited on any room temperature surface, e.g., conductors, insulators, plastics, fibers, and patterned surfaces, in a conformal fashion. The effects of deposition conditions, substrate type, and patterning on film morphology, nanostructure, and surface coverage will be highlighted. Energy storage application examples to be discussed include NiO on carbon for supercapacitors and CuO for conversion-type Li-ion batteries. The synthesis approach presented herein provides a general and tunable method to deposit a variety of functional and hierarchical metal oxide materials on many different surfaces.

Plasma Science and Technology Division
Room: 23 - Session PS-WeM

Advanced BEOL/Interconnect Etching

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, GeunYoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS-WeM1 Plasma Etch Considerations for EUV Quad-layer Patterning Stacks**, ***Angélique Raley***, TEL Technology Center, America, LLC, *J.C. Shearer*, *I.P. Seshadri*, *A. De Silva*, *J.C. Arnold*, *N. Felix*, IBM Research Division, Albany, NY, *H. Cottle*, *A. Metz*, TEL Technology Center, America, LLC

Continued scaling in semiconductor technology nodes has seen the rise of multi patterning for several critical layers, leading to higher costs, variability, and process complexity. EUV direct print patterning can alleviate and address some of these issues. The insertion of this technology was showcased in 2016[1] by the IBM Alliance for back end of the line (BEOL) metal trenches on their 7nm device. Exploratory efforts have now shifted to enabling the second generation of EUV patterning, targeting sub-36nm pitch resolution with single exposure. In current CAR-based EUV lithography, thin photoresist is used to prevent pattern collapse defectivity in dense line-space regions. This thin photoresist requires careful engineering of the hardmask and underlayer films below to minimize selectivity burden on etch budgets. This paper will first discuss the etch process design differences between current 36nm pitch EUV patterning and what is needed for sub-36nm pitch. Secondly, we will survey several thin hardmask materials and discuss their interactions with various plasma chemistries. For each material, the impact of both gas chemistry and tuning parameter on selectivity and resist roughness will be reviewed. Finally, continuous wave plasma etch performance will be contrasted with a quasi-ALE plasma etch process[1,2] as well as other plasma etch schemes designed to widen the patterning process window and enable successful pattern transfer into a typical BEOL metal patterning stack.

This work was performed by the Research Alliance Teams at various IBM Research Facilities

[1] Xie, VLSI, IEDM, p. 2-7, 2016

* **Coburn & Winters Student Award Finalist**

[2] Cottle et al. AVS 2016 Quasi-ALE Plasma Etching of EUV Photoresist for Contact Profile Control and PR Selectivity Improvement

[3] Vinayak et al. AVS 2014 Plasma Etch Considerations for Roughness Improvements during EUV and DSA Pattern Transfer using Mid Gap CCP

8:20am **PS-WeM2 Direct Metal Etch Evaluation for Advanced Interconnect**, ***Sara Paolillo***, *F. Lazzarino, N. Rassoul, D. Wan, D. Piumi, Z. Tokei*, IMEC

For many decades, the semiconductor industry could follow Moore's law by introducing innovative device architectures, smart design, new integration and patterning concepts, better tools and new materials. While industry is almost ready for high volume manufacturing of the 7nm technology node, new approaches are constantly being tested by research centers to enable further scaling down to the 5nm and 3nm technology nodes targeting respectively a metal pitch of about 32nm and 21nm. At such aggressive pitches, the effective resistivity of damascene Cu wires increases drastically due to both surface and grain boundary scattering but also due to the need of a Cu diffusion barrier that can't be scaled down. Besides the resistivity aspect, low-k damages induced by both plasma processing and barrier deposition contribute to the low reliability performance of damascene Cu interconnects.

In this context, alternative integration schemes exploiting direct metal etch technology and alternative metals like Ru have gained interest. A semi-damascene flow for instance can advantageously be used to overcome the aforementioned challenges. It consists of opening the vias into the low-k layer and filling them with a blanket metal deposition; connection are then created into the metal layer through direct etch. The empty trenches are finally either filled with low-k or used in an air gap configuration. This concept shows many advantages: it is suitable for a barrier-less integration, it prevents low-k damage and it allows for larger metal grain size. Regarding material selection, Cu is not a viable option considering the well-known difficulties in reactive dry Cu patterning. Ru is chosen as an alternative thanks to the ease with which it can be patterned using a conventional RIE process. Moreover, Ru line resistance is expected to go below Cu line resistance at CD below ~13nm, considering a line aspect ratio of 2. A further decrease in resistance can be expected with an increase in the Ru line aspect ratio.

In this work, we study the integration of Ru as a material for interconnect wires using a semi-damascene flow. Ru lines at 32nm pitch and with an aspect ratio of at least 2 are patterned using direct RIE targeting lines of 16nm and exploring a scaling extension down to 12nm. We will compare the electrical performances of Ru lines made from 3 different integration schemes. In one case, the patterns will be obtained using EUV single print lithography and in the other two cases, a 193i lithography will be employed defining the metal lines either from the spacers in the Anti Spacer Quadruple Patterning (ASQP) approach or from the tone inverted trenches in the SAQP approach.

8:40am **PS-WeM3 Evolution of Dielectric Etchers**, ***Hiromasa Mochiki***, Tokyo Electron Miyagi Limited, Japan **INVITED**

Plasma etchers have met stringent requirements of selectivity, profile, loading and uniformity to make shrinking of device dimensions possible. To that end, plasma etchers evolved from single frequency capacitively coupled plasma (CCP) to multiple frequency CCP, high density plasma (ICP, Microwave) and remote plasma sources. CCPs have been employed in dielectric etches due to it's ability to achieve high ion energies and low dissociation rate. Single frequency CCP evolved to CCP with magnetic enhancement and decoupled CCPs with high frequency on the top electrode or on the wafer. These knobs provided independent control plasma density and ion energy. Innovation in RF engineering enabled RF power to be split in different segments of electrodes to provide uniformity control and to eliminate standing wave effects. Recently, Direct Current Superposition (DCS) has been added to CCPs to alleviate differential charging, control C/F ratio in fluorocarbon plasmas and curing of resists. In addition to etching dielectric SiO2 and low-k materials, CCPs are employed in etching hard-mask etching process. For 7nm and beyond technology, the shrinking of critical dimensions (CD) without iso-dense loading is required. To meet this requirement, in-situ ALD + Etch is used. With Fusion of Etch and ALD, CD shrink with atomic precision for various patterns, without causing CD loading is achieved. In addition, uniformly control of the CD shrinkage amount across the wafer and Line Edge Roughness Improvement are demonstrated by ALD + Etch process. Process results will be presented to elucidate etch hardware evolution.

9:20am **PS-WeM5 Etch Residue Formation and Growth on Patterned Porous Dielectrics: Angle-resolved XPS and Infrared Characterization**, ***QuocToan Le***, *E. Kesters, F. Holsteyns*, IMEC, Belgium

Porous low-k dielectrics have been commonly used in micro- and nanotechnologies since the past decade. In back-end of line interconnect, the dielectric layer is typically patterned by dry etching through a photoresist or metal hard mask using fluorocarbon-containing plasmas, followed by electroplating of Cu inside the etched patterns. Residues are always formed during the pattern etching, regardless of the hard mask type.

This study focused on the types of residues generated during, and after, the plasma patterning of TiN hard mask/ porous low-k damascene stack. The porous dielectric s used in this study were CVD organosilicate glass (OSG) with target *k*-values of 2.2 and 2.55. Stacks of Si substrate/ OSG/SiO_2/TiN (from bottom to top) of 45 nm ½ pitch were prepared as test vehicles. Several methods commonly used for blanket surface characterization were applied for the patterned structure under study, including contact angle, Fourier transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Using fluorocarbon-based dry etch plasma to pattern the OSG, for both 45 nm ½ pitch stacks, etch residues were detected on the TiN surface, dielectric sidewall and bottom (Figure 1, after aging, Supplemental document). The XPS F1s core-level spectra collected from the patterned OSG consisted of two main components: a sharp peak centered at ~684.6 eV corresponds to F-Ti bonds and the peak at higher binding energy (chemical shift ~3.9 eV) can be assigned to C-F bonds. In order to have further insight into the residue location, XPS spectra were collected at various take-off angles (TOA, measured with respect to the surface normal) with the beam perpendicular to the low-k lines. While the polymer-based residues (CFx) are mainly detected on trench sidewall and bottom (measured at low TOA, Figure 2, Supplemental document), the metal-based residues (TiFx) are mainly formed on the top surface (at high TOA). For the high binding energy component, the apparent chemical shift recorded at low and high TOA's is estimated to be ~0.85 eV, suggesting the presence of organometallic-type residues close to the top surface.

The effect of moisture and aging time on the density of the residues were investigated. Ti-containing residues tended to grow upon aging. The saturation level of the growth appeared to depend on the amount of the residues initially present on the surface. In terms of residue removal, the effect of a subsequent plasma treatment (post-etch treatment) and/or a wet clean on the removal of these residues was also studied.

9:40am **PS-WeM6 Etch Challenges Associated with Sub-36nm Pitch BEOL EUV Patterning**, ***Jeffrey Shearer***, IBM Research Division, *A. Raley*, TEL Technology Center, America, LLC, *A. De Silva, L. Meli, I.P. Seshadri, R.K. Bonam, N.A. Saulnier, B. Briggs*, IBM Research Division, *T. Oh*, Samsung Electronics Co. Ltd., *A. Metz*, TEL Technology Center, America, LLC, *J.C. Arnold*, IBM Research Division

The rising cost of implementing EUV lithography is often cited as a major detractor for its adoption in future semiconductor technology nodes. The ability to directly print EUV levels with a single exposure not only alleviates some of the cost of processing but also many of the process challenges associated with multiple patterning techniques. However, scaling EUV technology, notably beyond 36nm pitch, comes with its own challenges. For example, constraints on resist thickness and hardmask material choices have emerged as unique etch challenges for BEOL patterning. Both new etch chemistries and novel etch techniques, such as the implementation of quasi-atomic layer etching and DC superposition, have proven invaluable in patterning beyond 36nm pitch.

We have demonstrated capability for EUV single exposure patterning beyond 36nm pitch using both trilayer and quadlayer patterning stacks. This paper will highlight benefits and challenges of each in terms of etch development. Specifically, SiARC-based patterning stacks will be compared to organic BARC-based quadlayer stacks with various hard layers in them. The introduction of each stack material was tested at 36nm pitch before transferring to sub-36nm pitch devices. Each pitch and stack has its own set of etch considerations, and we will address their impact on pattern transfer capability, CD process window, LER/LWR, the effort and methods necessary to overcome resist scumming, line end pullback, and others. An analysis of etch parameter selection will show how defectivity can be improved for each material stack. A programmed roughness structure allows detailed LER/LWR analysis for etch process tuning. Lastly, we will discuss the benefits and drawbacks of each patterning stack and present an outlook on material selection for next-generation sub-36nm pitch architecture.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:00am **PS-WeM10 ALD-SiO2 Chamfer-Less-Flow for Dual Damascene Integration**, ***Xinghua Sun***, *T. Yamamura, A. Metz, P. Biolsi*, TEL Technology Center, America, LLC, *H. Nagai, R. Asako*, Tokyo Electron Limited PCDC, Japan

In the traditional back end of line (BEOL) Dual Damascene structure integration, all-in-one-etch flow has been widely applied for successful interlayer metal connection. As technical node is being scaled down to 10/7nm, ever 5nm with lower K value (2.5), via chain chamfer profiles become more and more important to chip yield. However, once via mask organic is stripped off during all-in-one etch, chamfer corner extensively exposes to trench etching plasma damage resulted from radical or ion

bombardment. Therefore, chamfer corner can be etched much faster than trench, resulting in seriously rounded and chopped chamfer corner. In addition, ultra low K material can be damaged by some plasma like organic strip plasma. After the trench etch/wet clean and metallization, the rounded and chopped chamfer corner can cause electrical short, remarkably lowering yield and reliability. Regarding this point, it is a very critical goal to minimize such rounding/damage of chamfer as much as possible.

We here present an atomic layer deposition (ALD)-SiO2 chamfer-less Dual Damascene flow. In this flow, a few nanometer ALD-SiO2 film is deposited around via after via opening. The SiO2 pillar left on via sidewall plays the role to protect the chamfer corner from seriously chopping and damage while the following etching. According to different applications, this SiO2 pillar height is controllable and completely etched off while trench process. This can significantly improve the chamfer angle/profile. The ALD-SiO2 chamfer-less-flow has a few advantages. First, ALD oxide material can be uniformly deposited on via sidewall and easily etched off with trench process. Second, trench is not affected since the ALD-SiO2 is deposited before organic layer stripping. Third, it is a simple integration flow as only one extra SiO2 deposition step is added. The last one is to prevent electrical short between via chain and underneath metal, which improves the chip yield/reliability.

11:20am **PS-WeM11 Tone Reversal Technology Development Targeting Below 5nm Technology Node Applications**, ***Stefan Decoster***, *F. Lazzarino, X. Piao, N. Rassoul,* IMEC, Belgium, *Y. Fourprier,* TEL Technology Center, America, LLC, *D. Piumi*, IMEC, Belgium

For many decades, the semiconductor industry could follow Moore's law by introducing innovative device architectures, smart design, new integration and patterning concepts, better tools and new materials. While industry is almost ready for high volume manufacturing of the 7nm technology node, new approaches are constantly being tested by research centers to enable further scaling down to the 5nm technology node (N5) and below. In order to enable a number of these new integration approaches, there is a growing need for a well-understood and well-controlled tone reversal technology that consists of inverting the tonality of all structures present on the wafers, such as inverting ~20nm holes to blocks and sub-20nm lines to trenches, as well as large (micrometer-sized) structures such as alignment marks and overlay targets. The multiple Litho-Etch (LE) block patterning, the Self-Aligned Block (SAB) concept or the Direct Metal Etch (DME) approach are few examples of applications that advantageously integrate such tone reversal technology. A typical tone reversal flow consists of filling the patterns to be inverted with a material that could be either spin-coated or deposited. By means of dry etching or chemical mechanical polishing (CMP), the filling material is then thinned down to the top of the filled patterns which are finally selectively pulled out leaving the reversed patterns behind. A PECVD/ALD-type of filling would generally lead to the formation of voids between the patterns and to a low planarization performance requiring the use of an expensive CMP step that has a limited process window. Spin-coated materials are providing a good alternative to PECVD/ALD layers as they offer the possibility to achieve void-free filling and good planarization performance through material and process optimization. In this work, we focus on a fundamental understanding of the planarization properties of spin-coated materials. More specifically, the filling properties and planarization of different spin-coated materials (spin-on-glass, spin-on-carbon or spin-on-metal oxides) are screened in a selection of relevant matrix materials. By means of High Resolution Profiling, top-down and X-section Secondary Electron Microscopy the planarization properties are characterized as a function of pattern size, density and aspect ratio. Finally, the performances of the most promising tone reversal technologies are evaluated on concrete N5 and N3 applications like SAB and DME.

11:40am **PS-WeM12 Towards the Elimination of Ultra-Low *k* Ash Damage Using an *In Situ* Plasma Polymerized Film during Etch**, ***Katie Lutker***, TEL Technology Center, America, LLC

Ultra-low-*k* SiCOH films (ULK) are commonly used as an interlayer dielectric layer in the back-end-of-line. Unfortunately, as the industry moves towards new lower-*k* materials, particularly for the 7 nm node and beyond, not only does the extent of the damage caused by ash to the ULK increase, but so does the effect of damaged material on device performance. Such damage can adversely alter the feature profile and CD, RC response, and device lifetime and because of the nature of the plasma etch can be difficult to prevent. The reduction or elimination of such ash damage would facilitate the continuation of in-situ ash during the dielectric open process while opening the door to more novel integration schemes that are currently limited by the creation of a damaged layer. In order to reduce the damage, we have developed a process to deposit a plasma polymerized organic film *in-situ* during the etch process. The process utilizes a novel fluorine-free chemistry using a $C_xH_yN_z$ precursor to produce a conformal film in an etch chamber. The deposition process was optimized using patterned substrates such that the effects of the plasma ash on the sidewalls and feature bottom could be monitored and compared. Because the deposition step occurs in the etch chamber, the deposition and etch steps can be cycled such that even the feature sidewalls are constantly protected. By tuning the deposition and subsequent ash plasma parameters, the resulting damage to the ULK was significantly reduced through the use of the protecting polymer film.

12:00pm **PS-WeM13 Direct Metal Nanowire Patterning Using Ion Beam Etch**, ***Shreya Kundu***, IMEC, Belgium, *S. Dutta*, KU Leuven, IMEC, Belgium, *A. Gupta, G. Jamieson, D. Piumi, J. Boemmels, C.J. Wilson, Z. Tokei, C. Adelmann*, IMEC, Belgium

Scaling of metal lines to sub-10 nm dimensions is a pivotal driving force for progressing in the field of electronics and physics. Their fabrication by conventional lift-off/damascene approaches can be highly demanding. Some of the challenges which need to be circumvented for their creation are high resolution lithography of thinner resist and pattern transfer to form well-resolved lines/spaces. In addition, stress induced ruptures can form in the grain boundaries of the deposited metal film as the linewidth and grain size converge to similar dimensions. Here, we showcase an approach wherein we can directly pattern narrow metal lines with the use of relaxed dimension 248 nm optical lithography. Ru metal films of thicknesses ranging from 8-12 nm were deposited in a conformal way atop 300 nm wide (lines/spaces), ~7 µm long and 25 nm high patterned oxide (SiO_2) core. The oxide core height and the metal thickness can be varied to provide the flexibility of tuning the metal cross-sectional area. Ion beam etch (IBE) using Ar^+ ions was carried out to remove the film from the top and adjacent trenches of the oxide core, leaving behind long, continuous Ru lines of cross-sectional area <100 nm^2 along the oxide sidewalls. IBE works under the principle of physical momentum transfer (binary collision process) from the incident ions to the metal atoms which causes their eventual ejection from the substrate. Hence, unlike chemical etch, the physical etch process is not impacted by the change in grain size and grain boundaries of the metal. The cross-sectional area of the nanowires and its profile could be improved by controlling the Ar^+ ion accelerating voltage (50-400V) and time. TEM investigation revealed that the use of this ion bombardment based physical etch process didn't have an adverse impact on the metal crystallinity.

The Ru lines were electrically examined to estimate their performance as interconnects for advanced technology nodes. The electrical resistance yield achieved was >70%, indicating this physical etch process to be a robust method for such scientific studies. The fabrication method is not complex, compatible with the current silicon-based technology and can be extended to patterning of different metals and their alloys such as Ir, Rh amongst others.

References:

[1] L. G. Wen et al., ACS Appl. Mater. Interfaces, 2016, 8, 26119.

[2] S. Yasin, D. G. Hasko, H. Ahmed, Appl. Phys. Lett. 2001, 78, 2760.

[3] P. G. Glöersen, Journal of Vacuum Science & Technology 1975, 12, 28.

Plasma Science and Technology Division
Room: 22 - Session PS+SS+TF-WeA

Plasma Deposition

Moderators: Jeffrey Shearer, IBM Research Division, Albany, NY, Thorsten Lill, Lam Research Corporation

2:20pm **PS+SS+TF-WeA1 Correlation Between Ion Energies in CCRF Discharges and Film Characteristics of Titanium Oxides Fabricated via Plasma Enhanced Atomic Layer Deposition**, ***Shinya Iwashita***, *T. Moriya, T. Kikuchi, N. Noro, T. Hasegawa,* Tokyo Electron Limited, Japan, *A. Uedono*, University of Tsukuba, Japan

A plasma enhanced atomic layer deposition (PEALD) process for synthesizing titanium oxide (TiO_2) thin films, which allows to modify the film properties by tuning the ion energies of capacitively coupled radio frequency (CCRF) discharges, was performed. TiO_2 films were deposited via the oxidation of titanium tetrachloride using a typical CCRF discharge in argon/oxygen mixtures, and the energy distributions of ions hitting an electrode (wafer surface) during the deposition were adjusted by controlling the impedance of the electrode [1]. The wet etching rate of TiO_2 films shows a clear correlation with the mean ion energy; a higher mean ion energy realizes a higher value of the wet etching rate. The film characteristics are varied due to the balance between the oxidation and ion bombardment during the PEALD process. In a high mean energy condition, fine pores are formed in films due to the bombardment of high energetic ions, which was confirmed by the physical analyses such as positron annihilation spectroscopy. One can conclude that the energy control of ions in CCRF discharges is interpreted as tuning the oxidation and ion bombardment, both of which determine the film characteristics.

[1] K. Denpoh et al Proc.38th Int. Symp. Dry Process, 183 (2016).

2:40pm **PS+SS+TF-WeA2 Functionalized Titanium-Nitride Surfaces Formed by Femtosecond-Laser Processing**, ***David Ruzic***, *S. Hammouti, B.J. Holybee*, University of Illinois at Urbana-Champaign, *B.E. Jurczyk*, Starfire Industries

Thin films surfaces are playing an increasing role in the application of smart materials. This covers the improvement of surface properties like hardness, corrosion resistance, thermal, magnetic properties and so on depending on the application field. Many methods evolved for the preparation of thin films and coatings and among them the laser surface treatment. Since a decade, femtosecond laser micro-machining has been successfully introduced in industry for optic, surface wetting, biological or catalytic applications. The high precision achieved with femtosecond lasers for drilling or texturing purposes originates primarily from the limited heat affected zone which is greatly reduced compared to that of laser systems with longer pulse duration such as nano or picosecond. Moreover, ultrafast laser surface processing provides a simple way of nanostructuring and surface functionalization towards optical, mechanical or chemical properties. Indeed, irradiation of surfaces with short laser pulses of high intensity in a reactive atmosphere can result in a direct coating formation if the laser parameters are properly adjusted.

In this study, femtosecond laser processing of titanium surface in nitrogen (laser nitriding) has been investigated due to technological importance of nitrogen in metals and alloys for fusion applications. A two-step process consisting firstly to a femtosecond laser texturing of titanium surface under argon and then under nitrogen, both at atmospheric pressure, has been used. The laser treatment under argon has been proved to be efficient to remove most of the oxide layer which otherwise reduce the formation of titanium nitride. Several laser parameters for both laser treatments have been tested to obtain the best combination for the generation of titanium nitride. Beside chemical modifications of titanium surface, the formation of self-organized micro/nanostructures usually observed after irradiation in an ultrashort regime which result in topographic modifications are also of the high interest for wetting properties. Due to nonthermal effects involved in the ultrashort femtosecond processes the normal nitrogen diffusion process, as in the case of nanosecond laser nitriding. The titanium nitride layer produced by the femtosecond pulses most probably corresponds to nitride fall out from the recondensing plasma formed after the laser pulse above the irradiated surface, containing titanium and nitrogen ions and atoms.

3:00pm **PS+SS+TF-WeA3 Controlling the Thin Film Properties of Silica Synthesised by Atmospheric Pressure-Plasma Enhanced CVD**, ***Fiona Elam***, *A.S. Meshkova,* FOM institute DIFFER, Netherlands, *B.C.A.M. van der Velden-Schuermans, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., *M.C.M. van de Sanden, H.W. de Vries*, FOM Institute DIFFER, Netherlands

Atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) is an innovative technology that can be integrated into many existing manufacturing systems to facilitate the mass production of functional films; specifically encapsulation foils. These barrier films are essential to the flexible electronics industry, envisioned to protect devices such as flexible solar cells and organic light emitting diodes against degradation from oxygen and water.

Industrially and commercially relevant roll-to-roll AP-PECVD has been used to deposit silica thin films onto flexible polyethylene 2,6 naphthalate substrates by means of a glow-like dielectric barrier discharge using an air-like gas mixture. Single and bilayer films were evaluated in terms of their encapsulation performance, their chemical structure, the nature of their porosity and their morphology, with respect to the deposition conditions.

It was found that by increasing the plasma residence time and reducing the precursor (tetraethyl orthosilicate (TEOS)) flux, the specific input energy per TEOS molecule could be enhanced, which in turn resulted in the deposition of films with a lower intrinsic porosity. However, an input E/TEOS greater than 9 keV was found to limit the encapsulating performance of single layer barrier films, due to the creation of ~1 μm diameter pinhole defects. This restriction was overcome by the deposition of a semi-porous silica 'buffer' layer between the polymer substrate and silica 'barrier' layer. The buffer layer within the bilayer architecture acted as a protective coating to prevent excessive plasma-surface interactions that can occur during the harsh processing conditions necessary to generate dense barrier films. As a result, the bilayer films demonstrated exceptionally low effective water vapour transmission rates in the region of 2×10^{-4} g m^{-2} day^{-1}, values so far unprecedented for silica encapsulation barriers deposited at atmospheric pressure on flexible polymer substrates. Finally, regarding process throughput for the manufacture of silica thin films capable of protecting flexible solar cells, a 140% increase in processing speed was achieved for bilayer films with respect to 100 nm single layer barriers of equivalent encapsulation performance.

3:20pm **PS+SS+TF-WeA4 Plasma Information Based Virtual Metrology for Nitride Thickness in Multi-Layer Plasma-Enhanced Chemical Vapor Deposition**, ***Hyun-Joon Roh****, *S. Ryu, Y. Jang, N.-K. Kim, Y. Jin, G.-H. Kim,* Seoul National University, Republic of Korea

Advanced process control (APC) is required to assure the quality and throughput of plasma-assisted process. For this purpose, the process result of all wafers should be measured. However, direct metrology can measure only 1~3 wafers within a lot due to slow time response. To improve the speed of metrology, virtual metrology (VM) is alternatively adopted to support APC. VM can predict the process results close to real-time, since it predicts the process results by using statistical methods based on equipment engineering systems (EES) and sensor variables. However, previously developed VMs face the degradation of prediction accuracy as the chamber wall condition drifts in long-term process. This robustness issue is originated from that the used input variables of VM cannot recognize the drift of chamber wall condition. To enhance the robustness even in a process with severe drift of chamber wall condition, we propose PI-VM that uses plasma information (PI) as input variables of statistical methods. Experimental application of PI-VM is performed to predict the nitride film thickness in multi-layer plasma-enhanced chemical vapor deposition (PECVD) for 3D NAND fabrication which has a severe drift of chamber wall condition. PI variables are composed of the chamber wall condition (PI_{Wall}) and property of bulk plasma (PI_{Plasma}) considering plasma-surface interaction. Each PI variable is decomposed from N_2 emissions in optical emission spectroscopy (OES) by analyzing them based on optics and plasma physics. Then, PI-VM is constructed by implementing PI and EES variables to partial least squares regression (PLSR). Compared to conventional VM, PI-VM improves the robustness more than twice in long-term variation by implementing PI_{Wall} on PLSR. Also, evaluation of the ranking of variables on PI-VM shows that the robustness is improved by decomposing PI_{Wall} and PI_{Plasma} from OES based on optics and plasma physics. This result showed that an effective VM model for plasma-assisted process can be constructed by making phenomenological-based, statistical-tuned VM model that recognizes the

*** Coburn & Winters Student Award Finalist**

drift of chamber wall condition and property of plasma separately, based on optics and plasma physics.

4:20pm **PS+SS+TF-WeA7 Sidewall Effects in the Modulation of Deposition Rate Profiles of a Capacitively Coupled Plasma Reactor**, ***Hojun Kim***, Samsung Electronics Co. Ltd., Republic of Korea **INVITED**

In the recent semiconductor industry, plasma-enhanced chemical vapor deposition (PECVD) using capacitively coupled plasma (CCP) is often chosen to coat a thin uniform film with a high production efficiency. Since inside of a CCP reactor, a discharge volume is radially surrounded by a sidewall, the modulation of the sidewall surface can contribute to controlling distributions of plasma variables. In this study, we thus investigate the sidewall effects by varying the electrical condition of the sidewall from grounded to dielectric. In the cases with the dielectric sidewalls, a cylindrical insulator with a grounded exterior surface is adopted, and then its radial thickness is additionally varied from 2 mm to 45 mm. As an example for the particular case of PECVD, SiH_4/He discharge during deposition of an amorphous hydrogenated silicon (a-Si:H) film is simulated using a two-dimensional fluid model. The cases with the thick insulators have more uniform distributions of the plasma variables than the case with the grounded sidewall or the case with the thin insulator. An increase of the showerhead radius also improves a distribution uniformity because non-uniformity sources of the plasma distribution are set further away from the electrode edge.

5:20pm **PS+SS+TF-WeA10 Linear Magnetron Magnetic Field Optimization for HiPIMS Industrialization**, ***Ian Haehnlein***, *J. McLain, B. Wu, I. Schelkanov*, University of Illinois at Urbana-Champaign, *B.E. Jurczyk*, Starfire Industries, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HiPIMS) has time and time again been proven to provide superior film qualities over direct current magnetron sputtering (DCMS) due to increased ion fraction at the substrate. Throughput however is decreased due to the increase in return of sputtered target material [1]. Work done previously at the Center for Plasma Material Interactions (CPMI) at the University of Illinois Urbana-Champaign by Raman et al. introduced the Tripack for a 4" circular magnetron. This magnet configuration features three distinct racetracks with magnet fields tuned to allow electron escape from the magnetron magnetic field during high power pulses [2]. This was used in a linear magnetron to increase the deposition rate of HiPIMS. McLain et al. has shown using a 5x11" linear magnetron a decrease in the confinement parameter of during DC from 6 using a conventional magnet pack to 3 using the Tripack designed for a linear magnetron. Deposition rates for HiPIMS using Tripack increased deposition rates over the conventional pack by ~25% for copper. In the 1.5kW case the HiPIMS discharge using the Tripack was ~1nm/s greater than that of DCMS using the conventional magnet pack. Triple Langmuir probe measurements at the substrate verified an increase of several orders of magnitude over the conventional pack, supporting the theory that a decreased electron confinement would increase deposition rate, further supported by an increase in ion-neutral fraction at the substrate from ~12% to 35% measured at the substrate surface. Due to non-uniform redeposition on the target surface the, preferentially towards the center, that the outer racetracks eroded faster and subsequentially had stronger magnetic fields at the target surface. The inner racetrack fails to ignite, causing uneven erosion of the target. It is proposed that by creating a serpentine magnet pack which utilizes the reduced confinement parameter seen in the Tripack with only one racetrack as to confine electrons evenly over the target surface. Deposition rates, electron densities, and ion-neutral fractions for the improved magnet pack are provided in this work. These values are presented with and without the use of a positive polarity modified waveform controlling ion deposition energy independent of the substrate for a better controlled deposition on insulators or temperature sensitive materials.

5:40pm **PS+SS+TF-WeA11 Investigating the Effect of the Substrate at Short Deposition Times for Plasma Polymerised Films**, ***Karyn Jarvis***, *N.P. Reynolds*, Swinburne University of Technology, Australia, *L.D. Hyde*, Melbourne Centre for Nanofabrication, Australia, *S.L. McArthur*, Swinburne University of Technology and CSIRO, Australia

Plasma polymerization modifies surfaces via the deposition of a thin film containing specific functional groups. The organic monomer is introduced into the chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma. Plasma polymerization is typically referred to as 'substrate independent', but is this true for short deposition times? Does the substrate conductivity, chemistry or roughness influence the early stage deposition of plasma polymer films? In this study, plasma polymerized acrylic acid (ppAAc) and allylamine (ppAA) were deposited onto glass, silicon, gold and fluorinated ethylene propylene (FEP) substrates for deposition times of 10 to 600 seconds. Surface chemistry was investigated using X-ray photoelectron spectroscopy while surface roughness was determined using atomic force microscopy. Film thickness measurements were made by spectroscopic ellipsometry and wettability determined via contact angle measurements. Different contact angle behaviours were observed between the deposition of ppAAc and ppAA films, while different substrates resulted in different contact angle trends for ppAA. For ppAAc films deposited for 10 seconds, all substrates became more hydrophobic (80-100°) and was proposed to be due to 'island' film formation, which would increase surface roughness and therefore increase hydrophobicity. For ppAA films deposited for 10 seconds, the contact angles of all substrates except FEP increase/decrease to 60-70° and do not significantly change as deposition time increase. Such behaviour suggests the ppAA films may deposit continuously from the start, unlike ppAAc which may initially form film islands. Unlike all the other substrates, FEP showed the same behaviour for both monomers, suggesting initial island formation for both monomers. These initial results suggest that for short deposition times, the underlying substrate does have some influence on the formation of plasma polymerized films.

Plasma Science and Technology Division
Room: 23 - Session PS-WeA

Modeling of Plasmas

Moderators: Kostya (Ken) Ostrikov, Queensland University of Technology and CSIRO, Richard van de Sanden, DIFFER

2:20pm **PS-WeA1 TSV Etch Plasma Modelling from Chamber to Feature**, ***Sebastian Mohr***, Quantemol LTD, *S. Rahimi, A. Dzarasova*, Quantemol LTD, UK

A key goal of the presented research project PowerBase is to produce new integration schemes which enable the manufacturability of 3D integrated power GaN smart systems with high precision TSV etched features. This project is a collaboration of 39 partners focused on exploring novel materials and manufacturing processes optimisation and testing. Quantemol's contribution to the PowerBase project includes the simulation of the Rapier reactor built by SPTS presented here. This tool allows control of the homogeneity of particle fluxes to the wafer via two independently controlled coils and two independently controlled nozzles. In this project, the Rapier is used to etch through Si wafer via the BOSCH process. By combining simulation and experiment, we look for the parameter settings, which ensure homogeneous etch rates and features with a minimal amount of scalloping. This presentation includes the simulations of the reactor in both SF_6 and C_4F_8 performed with Q-VT/HPEM as well as feature profile simulations. Due to the complicated chemistries, the non-trivial geometry of the reactor, and limited diagnostics, simulating the Rapier is an arduous task. As this presentation will show, we managed to achieve excellent agreement between experimentally and computationally obtained surface rates. The reactor simulation employs fluid techniques to calculate the particle densities and fluxes as well the electric fields and a Monte Carlo Simulation of the reactive species, both neutrals and ions, to obtain the distribution of these particles at the wafer with regards to both energy and angle (IEADFs). FInally, the IEADFs and particle fluxes are used in the feature profile model, which alternates between the polymer deposition process in C_4F_8 and the etching process in SF_6 , which in this case is almost exclusively driven by the chemical etch of silicon by fluorine radicals. Due to the isotropic nature of the chemical etch, a certain amount of scalloping is to be expected. The simulation identified the effect of key parameters such as the ICP and rf-bias power on the feature profile, as well as the homogeneity of particle fluxes. These insights were transferred to the experiment with the final goal to achieve the optimal combination of radially homogeneous surface rates, smooth features, and process time. This presentation highlights the challenges of simulating the Rapier, comments on the agreement between simulation and experiment, and analyses the effect of parameter variations such as power and gas flow on the flux homogeneity and feature profile.

2:40pm **PS-WeA2 Global Model based Framework for Prediction of Ion Energy Distributions Under Pulsed RF-bias Conditions in Plasma Etching Processes**, ***Shogo Sakurai***, ET Center, Samsung R&D Institute Japan, *S. Lim*, Samsung Electronics, Korea, *R. Sakuma, S. Nakamura, H. Kubotera, K. Ishikawa*, Samsung R&D Institute Japan, *K. Lee*, Samsung Electronics

Prediction of ion energy distributions (IEDs) under real process condition is one of the critical issues in plasma etching processes of micro-fabrication of semiconductor devices. In this study, we developed global (volume-averaged) model based framework to predict the IEDs under the real conditions with pulsed RF bias, dual/triple frequencies, and the high power sources. By employing global model as the core module, our framework achieves not only strong robustness compared with existing higher

dimensional equipment simulators for the severe conditions, but also acceptable simulation time as daily simulator for extensive low pulse frequency such as 100Hz. Furthermore, our framework was applied to wide variety of plasma reactors: inductively coupled plasma, capacitively coupled plasma (CCP), and microwave-excited surface wave plasma, by cooperation with electron heating model corresponding to the reactor type and the radio-frequency (RF) sheath model. On the other hand, the framework requires larger computational cost to obtain the results than original global model of steady state problems. Thus, our effort was much paid to reduce the time by utilizing numerical algorithms such as adaptive time stepper, hybrid time-integrator, etc. Especially, employed RF sheath model was expressed by one-dimensional fluid equation for ionic species which can be solved numerically by Runge-Kutta integration scheme; the integration also demands large computational cost due to the self-consistent coupling to equivalent circuit of RF biased substrates. Therefore, some sort of evaluation way of the model was needed for the reduction. Actually, the sheath model is used to calculate sheath width only on our model for evaluation of the sheath capacity. Fitting function to the numerical solution was employed to evaluate the value quickly. The obtained function has same asymptotic behavior as Child-Langmuir law for high potential drop limit. Furthermore, the curve of the function well reproduces the numerical solution for entire ranges of the potential drop where past analytical formula failed to reproduce. By using the function, we found that the simulation gains the speed by 39.1 times for pulsed dual RF CCP plasma with Argon gas compared to the unused case. The expression of the function was also extended to the numerical solutions of the electronegative plasma such as Cl_2 gas to gain the application range.

3:00pm **PS-WeA3 Understanding Particle-Surface Interactions and Their Importance in Plasma Processing: a Plasma Modelling Perspective**, ***Andrew Gibson***, *S. Schroeter*, *D. O'Connell*, *T. Gans*, University of York, UK, *M.J. Kushner*, University of Michigan, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France **INVITED**

Low-temperature plasmas are widely used in a number of important applications. Specific examples include the etching of nanoscale structures in the semiconductor industry, electric propulsion of spacecraft, and as reactive species sources in biomedicine. In all of these applications, the plasma is bounded by surfaces and as a result, particle-surface interactions play a crucial role in defining its properties. These interactions act as sources and sinks of charged and neutral particles and enable energy transfer processes that heat and cool the plasma. As such, particle-surface interaction processes can influence all aspects of the plasma dynamics, and a proper understanding of their effects is crucial to optimizing a given application.

However, for a given plasma-surface combination a complete picture describing all possible particle-surface interaction processes is almost never known. This is a major reason why numerical simulations of low-temperature plasmas, where probabilities for various particle-surface interactions are used as boundary conditions, are often challenged to predict the results of experimental investigations. The work presented here seeks to provide insights into several key particle-surface interaction processes occurring in prominent applications of low-temperature plasmas using a combination of zero- and two-dimensional numerical simulations. In particular, the role of atomic neutral species surface recombination, excited species surface quenching, neutral thermal energy accommodation and electron- and ion-induced secondary electron emission probabilities in defining the properties of low-temperature plasmas will be discussed.

Examples of the importance of these particle-surface interactions in both low-pressure plasma sources, used in the semiconductor industry for etching processes, and atmospheric pressure micro-plasmas, used as radical sources in biomedicine, will be presented. It was found that surface processes play a key role in both examples and strongly affect plasma parameters important for applications. In the low-pressure case, this includes the neutral-to-ion flux ratio, a key parameter for precision etching processes. At atmospheric pressure, the densities of radical species and the overall chemical composition of the plasma, key parameters for interactions with biological tissue, are found to be particularly affected. In each example, areas where particle-surface interactions may be harnessed to optimize applications through the tailoring of surface properties will be highlighted.

Funding through the LABEX Plas@Par project, ANR-11-IDEX-0004-02 and UK EPSRC Manufacturing Grant (EP/K018388/1) is acknowledged

4:20pm **PS-WeA7 Investigation of Pulsed $Ar/O_2/CF_4$ Capacitively Coupled Plasmas**, ***Wei Tian***, *S. Rauf*, *K.S. Collins*, Applied Materials, Inc.

High selectivity has become a critical requirement for many etching processes during microelectronics fabrication. These processes require good uniformity (both etch rate and critical dimensions) in addition to high selectivity. To meet these challenges, pulsed capacitively coupled plasmas (CCPs) have been introduced due to their ability to better control the flux of ions and radicals to the substrate as well as the energy of the ions incident on the substrate. By pulsing the plasma, one can more effectively modulate the electron energy distribution and the electron impact source functions of reactive species compared to traditional methods.[1,2] Pulsing introduces many additional control variables to already complicated etch processes. In addition, a variety of pulsing schemes are possible in multi-frequency CCPs. To optimize the pulsed CCPs processes, understanding of the transients during a given pulse is the key.

In this work, we will investigate the pulsed $Ar/O_2/CF_4$ CCPs using results from a 2-dimensional plasma equipment model.[3] We consider single and dual frequency CCPs, and both single source and synchronous pulsing schemes are investigated. The ignition of the plasma is influenced by the ramp-up of the applied voltage. An overshoot in electron density, electron temperature as well as in emission during the ignition is observed. Depending on the pulse frequency and duty cycle, the plasma during a pulse can be influenced by the previous pulse. The metastable states have a lifetime of milliseconds and are able to accumulate pulse-by-pulse. Through Penning ionization of metastable states, electron and ion densities are affected. The after-glow phase is important for controlling of ion flux and energy, and depends on the voltage decay and sheath collapse. The modeling results are also compared to experimental measurements for validation.[4]

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4:40pm **PS-WeA8 Modeling of Silicon Etching using Bosch Process: Effects of Oxygen Addition on the Plasma and Surface Properties**, ***Guillaume Le Dain***, STMicroelectronics / CNRS-IMN, France, *A. Rhallabi*, Cnrs - Imn, France, *S. Elidrissi*, University of Nantes, *C. Cardinaud*, *A. Girard*, Cnrs - Imn, France, *F. Roqueta*, *M. Boufnichel*, STMicroelectronics, France

Bosch process is currently used for semi-conductors devices manufacturing. This technique performs high aspect ratio features by alternating SF_6 and C_4F_8 plasma pulses. These features are needed for some micrometric scale systems such as Microelectromechanical Systems (MEMS) and System in Package (SiP). One of the problem encountered in silicon etching under Bosch process is the difficulty to minimize the scalloping effect characterized by the propagation of the ripples along the sidewall and to maintain a high etch rate.

Usually, a pure SF_6 plasma pulse for etching step and pure C_4F_8 plasma pulse for deposition step are used in silicon Bosch process. The aims of our study are to analyze the effect of oxygen addition to both SF_6 and C_4F_8 plasmas pulse on the silicon etching profile evolution and to understand how the oxygen could improve the etching anisotropy and minimize the scalloping effect. Indeed, previous works reveal that the addition of oxygen to SF_6 plasma for silicon etching under cryogenic process contributes to the sidewall passivation of etched silicon and thus to the improvement of the anisotropy [1]. In this context, we have added O_2 gas to our SF_6 and C_4F_8 plasmas module as well as sheath and surface modules of silicon etching simulator. This is to investigate its effect on the silicon etching profile evolution under Bosch process [2]. Our etching simulator is composed of three modules: 0D plasma kinetic module, 2D sheath module and 2D surface module. It allows the prediction of the silicon etching profile evolution as a function of the operating conditions such as power, pressure, flow rate, plasmas pulses times and bias.

The effects of $\%O_2$ on the electrical and kinetic properties of plasmas are analyzed. Moreover, its impact on the silicon etching profile evolution under the mask is presented.

Comparisons between the simulation and the experiments give satisfactory agreements for both plasma discharges and silicon etching profiles.

[1] R Dussart, T Tillocher, P Lefaucheux and M Boufnichel*J. Phys. D: Appl. Phys.***47** 123001 (2014)

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5:00pm **PS-WeA9 A Mixed Mode Parameter/Physical Driven Particle-in-cell (PIC) Code for Capturing Transient Response and Evolution Behavior of Laboratory Plasma**, ***Noel Lauer***, *N.J. Ianno*, University of Nebraska-Lincoln

A baseline *1d3v* full particle-in-cell (PIC) code has been modified extensively and is described. Modifications include the addition of a *local densityadjustment* (LDA) to the Monte-Carlo-Collision (MCC) algorithm to facilitate the study of plasma transients due to external pulsed stimulus and evolution behavior of plasma in general. The LDA-MCC adjusts for

conditions involving transient volume density distributions and population inversions, collisions outside the sputter injected material wavefront, zero population cells, extreme volume density gradients, and collisional vs. colliding species role reversals. Additional modifications were made to accommodate collisional interactions between the working gas neutrals (WG), ions (WG^+), and electrons (e^-) with cathode target material neutrals (T_n) and ions (T^+). The MCC was further altered to distinguish WG fast neutrals (WG_{fn}) and excited atoms (WG^*) to support de-excitation and Penning collisions important in high power impulse magnetron sputtering (HiPIMS). A comparative summary of particle-particle interactions supported vs. the baseline code are shown in Table 1 supplemental. Further changes were made to support parameter, physical, and mixed mode driven simulation regarding secondary emission coefficients (SEEC), target emission coefficients (TAEC), and their underlying implementation at the cathode. A physical driven model to support electron emission δ_e and a parameter driven target ion sticking coefficient has also been incorporated at the anode. Further revisions were made to accommodate SEECs and TAECs greater than 100% requiring changes to the charge adjustment algorithm. Finally, the particle mover and injection push algorithms were modified to support a decaying magnetic field B_z parallel to and sourced from the cathode.

When new material is introduced via sputter injection or HiPIMS is utilized, new material wavefronts and locally high volume densities can arise, Fig. 1 supplemental, causing incorrect collision statistics if treated as a uniformly distributed density throughout the plasma. Furthermore, large numbers of zero population cells can exist for individual species for periods of time during plasma evolution. These characteristics can produce collision results where source material is non-existent, Figs. 2-3 supplemental, and infer more collisions than existing source material. These discrepancies can be insignificant after the plasma has equilibrated but are unacceptable when studying transient behavior or the details of plasma evolution. The LDA-MCC makes adjustment for these scenarios.

5:20pm **PS-WeA10 Investigating Mode Transitions in Pulsed Inductively Coupled Plasmas**, ***Steven Lanham***, *M.J. Kushner*, University of Michigan

Pulsing the power applied to inductively coupled plasma (ICP) systems has beneficial effects, such as lowering average ion energies and customizing the flux of reactive species to surfaces [1]. With pulsed plasmas being increasingly used in semiconductor fabrication, more of the processing time is in a transient regime. For example, in many ICP systems pulsing the power repeatedly transitions between electrostatic (E-mode) power deposition at the start of a power pulse and inductive (H-mode) power deposition later during the power pulse [2]. This transition results from the large variation of the electron density, particularly for electronegative gas mixtures, and plasma impedance during a pulse. For the highly electronegative gases often used for processing, the plasma can essentially extinguish in the afterglow of a pulse and require reigniting at the start of every pulse.

In this paper, we discuss mode transitions for power deposition in pulsed ICP systems based on results from a computational investigation. The Hybrid Plasma Equipment Model (HPEM), a 2-dimensional plasma multi-fluid model [3], was used to simulate the consequences of the E-H transition resulting from capacitive coupling in pulsed ICPs. We found that for highly electronegative gas mixtures, such as Cl_2 at a few to tens of mTorr, the power initially applied at the beginning of a pulse is essentially purely capacitive. The dominance of sheath centric power deposition during startup can then launch electrostatic waves into the plasma, an outcome that is sensitive to antenna frequency and pulse repetition frequency. Choosing to operate with a ramped current or ramped power at the onset of a pulse can, in some instances, constrain operation to E-mode or allow a faster transition from E- to H-mode. The pulse power format has a first order effect – controlling current or controlling power – on the E-H transition, and the stability of the plasma.

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This work was supported by the National Science Foundation and the Department of Energy Office of Fusion Energy Science.

5:40pm **PS-WeA11 Science of Plasma-Surface Interaction for Modern Semiconductor Process Technologies**, ***Satoshi Hamaguchi****, *K. Karahashi*, Osaka University, Japan **INVITED**

The fast development and rapidly spreading use of Information and Communication Technologies (ICT) worldwide are firmly founded on the continuing development of semiconductor device technologies. With an increasing demand for higher integration density of large-scale integrated (LSI) circuits with lower energy consumption, device sizes continue to shrink, their structures become more complex (such as those of 3D multigate fin FETs), and unconventional materials (such as magnetic materials for MRAMs) are used for semiconductor devices. Challenges for plasma processing technologies used for LSI device fabrication therefore lie in the development of new plasma chemistry that allows processing with atomic-scale accuracy for existing as well as new materials used for crucial parts of semiconductor devices. Processing with atomic-scale accuracy is required to minimize material damages induced by ion bombardment, which means more chemistry-driven, rather than physical-sputtering driven, processes must be employed. For the development of plasma etching chemistry, the guiding principle is to find volatile molecules that can be formed from materials to be etched. However, unlike silicon or germanium based materials, which can be etched by the formation of volatile halides, most metal or metal oxides do not form volatile molecules under low-pressure plasma conditions. For example, the formation of volatile metal-organic complexes (such as metal carbonyls) from a metal or metal oxide surface is unlikely to occur in a low-pressure plasma as their coordinate covalent bonds are so weak that they could be easily broken by ion bombardment. The authors have analyzed etching chemistries of various materials, such as metal oxides, magnetic metals, amorphous carbon, as well as Si-based materials, using multi-beam experiments [1] and molecular dynamics (MD)/first-principle quantum mechanical (QM) simulations. In this work, we shall summarize our recent work on etching mechanism analyses and attempt to predict the future direction of process development.

References

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*** PSTD Plasma Prize Winner**

Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-ThM

Atomic Layer Etching I

Moderators: Andrew Gibson, University of York, UK, Saravanapriyan Sriraman, Lam Research Corporation

8:00am **PS+NS+SS+TF-ThM1 Strategies to Control the Etch per Cycle During Atomic Layer Etching of SiO_2 and SiN_x**, ***Ryan Gasvoda***, Colorado School of Mines, *S. Wang*, *E.A. Hudson*, Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

Decreasing device dimensions and the incorporation of increasingly complex 3D architectures place new constraints on conventional plasma processing techniques. One method to address the limitations of conventional etching is atomic layer etching (ALE) which can provide low damage and atomic-scale etch control. ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si-based dielectrics. In this study, we have explored the atomistic-level details of an SiO_2 and SiN_x ALE process consisting of a hydrocarbon-containing precursor dose, CF_x deposition from a C_4F_8/Ar plasma, and an Ar plasma activation step in which the CF_x film is activated and the underlying substrates are etched. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions and film composition as well as the net film thickness during the deposition and etching steps.

Sequential cycles of ALE of SiO_2 show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC is from excess CF_x that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the CF_x deposition onto the SiO_2 film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half-cycles of twice the length are employed, which allows for the removal of CF_x from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions.

To further control the EPC, a hydrocarbon precursor prior to the start of ALE retards the EPC. A broad feature centered at ~1,400 cm^{-1} builds up on the surface with increasing hydrocarbon dose frequency and cycle number, which is assigned to a carbonaceous film of CH_xF_y. The film acts as a blocking layer which prevents the activation of CF_x at the CF_x/SiO_2 interface and thus limits SiO_2 etching. No graphitic carbon buildup is observed. However, increasing the Ar plasma half-cycle length limits the buildup of the CH_xF_y film and increases the EPC. Using the same baseline processing conditions as ALE of SiO_2, ALE of SiN_x leads to a carbonaceous film buildup of both CH_xF_y and nitrile species at ~2,225 cm^{-1} which accumulates over cycle number and eventually leads to an etch stop. A longer Ar plasma half-cycle limits the accumulation of the CH_xF_y film and the EPC drift. The addition of a hydrocarbon precursor retards the EPC in a similar fashion as observed on the SiO_2 film.

8:20am **PS+NS+SS+TF-ThM2 Enabling Atomic Layer Etching of Magnetic and Noble Metal Alloys**, ***Nicholas Altieri****, *E. Chen*, University of California, Los Angeles, *J.K. Chen*, Lam Research Corporation, *J.P. Chang*, University of California, Los Angeles

Etching of magnetic and noble metals alloys utilized in ferromagnetic thin films crucial to the operation of magnetic memory has created a processing bottleneck, due to their chemically resistant nature. Widely-used etch techniques, including noble ion sputtering, exhibit limited success at patterning high aspect ratio features as well as a lack of selectivity. Furthermore, as feature sizes shrink, the demand for atomic level precision in patterning increases. A generalized strategy has been developed to enable dry etch processes shown to be effective for patterning elemental and alloyed metal thin films through the use of surface modification. Controlling the thickness of the modified layer allowed for direct control of the amount of material removed, indicating that this process would be viable for achieving atomic layer etch.

The etch of Co and Pt, elements commonly used in the magnetic memory stack, as well as ferromagnetic alloys CoPt and $Co_{30}Fe_{45}B_{25}$ were studied in this work. Inductively coupled oxygen plasma was utilized for surface modification, and organics including oxalic acid, formic acid, acetylacetone, and hexafluoroacetylacetone were investigated as chemical etchants.

Pt, Co, CoPt, and CoFeB thin films were first studied using continuous exposure to organic solutions. Pt showed no etch beyond the removal of a thin layer of native oxide. CoPt and CoFeB were shown to etch at rates up to 10 nm/min in formic acid solutions without plasma modification. Upon translation to the gas phase, where the concentration of organics was substantially lower, no etch was observed across all materials when continuously exposed to organic acid vapor.

Plasma oxidation was then utilized to chemically modify the surface through generation of directional metal-oxide bonding prior to treatment with organics. Subsequent exposure to formic acid solution indicated preferential and complete removal of metal oxides. A dual-step dry etch process consisting of plasma oxidation and organic vapor dosing was then developed which exhibited etch rates of 0.5, 2.8, 1.1, and 1.8 nm/cycle for Pt, Co, CoPt and CoFeB, respectively, and removing metallic oxides.

In formic acid solution, PtO_2 exhibited infinite selectivity to Pt, while oxidized CoPt and CoFeB were observed to have selectivities of 6.4 and 3.1, respectively, compared to their unoxidized counterparts. In the vapor phase, each oxidized material exhibited nearly infinite selectivity to each corresponding metallic film. Coercivity values (H_c) of 20 and 3.5 Oe were measured for Co and CoFeB before processing conserved to up to 99% of their original pre-processing values.

8:40am **PS+NS+SS+TF-ThM3 Directional Atomic Layer Etching: First Principles, Modelling and Applications**, ***Thorsten Lill***, *K. Kanarik*, *I.L. Berry*, *S. Tan*, *Y. Pan*, *V. Vahedi*, *R.A. Gottscho*, Lam Research Corporation **INVITED**

Atomic layer etching (ALE) has recently been introduced into manufacturing to produce 10 nm logic devices. ALE is an etching technology that deploys time or space separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most prominent property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness.

As compared to conventional plasma etching, step separation in ALE also offers a simplified system in which to study the etching mechanisms based on first principles. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach as well as experimental results.

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9:20am **PS+NS+SS+TF-ThM5 Thermal Atomic Layer Etching of VO_2 Using Sequential Exposures of SF_4 and Either $Sn(acac)_2$ or BCl_3**, ***Jonas Gertsch***, *V.M. Bright*, *S.M. George*, University of Colorado Boulder

Thermal atomic layer etching (ALE) is based on sequential self-limiting thermal reactions [1]. Thermal ALE offers a precise and gentle etching procedure and has been demonstrated for many materials including Al_2O_3, HfO_2, ZnO, ZrO_2, SiO_2 and AlN [1,2]. This study developed thermal ALE processes for vanadium oxide (VO_2). VO_2 has a metal-insulator transition at ~68 °C and is useful for thermochromic films and heat-switching devices. The initial VO_2 films were deposited using VO_2 atomic layer deposition (ALD) with tetrakis(ethylmethylamino) vanadium(IV) (TEMAV) and H_2O as the co-reactants at 150 °C.

The VO_2 films were etched using sequential exposures of sulfur tetrafluoride (SF_4) and either tin(II) acetylacetonate ($Sn(acac)_2$) or boron trichloride (BCl_3) at temperatures ranging from 150-250 °C. *In situ* quartz crystal microbalance studies were used to monitor film growth and etching during the ALD and ALE reactions. The VO_2 etching mechanism using SF_4 and $Sn(acac)_2$ is observed to occur by fluorination and ligand-exchange reactions [1]. The SF_4 exposures yielded mass gains that were consistent with fluorination of VO_2 to VF_4. The $Sn(acac)_2$ exposures then led to mass losses that were attributed to ligand-exchange reactions that produced volatile acetylacetonate reaction products. VO_2 ALE etch rates increased with temperature from 0.04 Å/cycle at 150 °C to 0.27 Å/cycle at 225 °C.

*** Coburn & Winters Student Award Finalist**

A different reaction mechanism was observed for VO_2 ALE using SF_4 and BCl_3. The SF_4 exposures yielded mass losses at all temperatures that were not consistent with simple fluorination of VO_2 to VF_4. The BCl_3 exposures produced mass losses at higher temperatures and slight mass gains at 150 °C. The etching of VO_2 by SF_4 and BCl_3 is believed to occur by a "conversion-etch" mechanism [2]. In the "conversion-etch" mechanism, BCl_3 converts the surface of VO_2 to a thin B_2O_3 layer. SF_4 can then remove the B_2O_3 layer to produce volatile BF_3 and SO_2. The VO_2 etch rates increased with temperature from 0.06 Å/cycle at 150 °C to 1.9 Å/cycle at 250 °C.

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9:40am **PS+NS+SS+TF-ThM6 Atomic Layer Etching of MoS_2 for Nanodevices**, ***KiSeok Kim***, *K.H. Kim, Y.J. Ji, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Among the layered transition metal dichalcogenides (TMDs) that can form stable two-dimensional (2-D) crystal structures, molybdenum disulfide (MoS_2) has been intensively investigated due to its unique properties in various electronic and optoelectronic applications with different band gap energies from 1.29 to 1.9 eV as the number of layers is decreased. To control the MoS_2 layers, atomic layer etching (ALE) (which is a cyclic etching consisting of a radical-adsorption step such as Cl adsorption and a reacted-compound desorption step via a low-energy Ar^+-ion exposure) can be a highly effective technique to avoid inducing damage and contamination that occur during the cyclic steps. In this study, for the MoS_2 ALE, the Cl radical is used as the adsorption species and a low-energy Ar^+ ion is used as the desorption species. A MoS_2-ALE mechanism (by which the $S_{(top)}$, $Mo_{(mid)}$, and $S_{(bottom)}$ atoms are sequentially removed from the MoS_2 crystal structure due to the trapped Cl atoms between the $S_{(top)}$ layer and the $Mo_{(mid)}$ layer) is reported with the results of an experiment and a simulation. A monolayer MoS_2 field effect transistor (FET) fabricated after one-cycle of ALE of a bilayer MoS_2 FET exhibited electrical characteristics similar to a pristine monolayer MoS_2 FET indicating no electrical damage on the monolayer MoS_2 surface after the ALE.

11:00am **PS+NS+SS+TF-ThM10 Ge Atomic Layer Etching for High Performance FinFET**, *W. Mizubayashi*, AIST, Japan, *S. Noda*, Tohoku University, Japan, *Y. Ishikawa, T. Nishi*, AIST, Japan, *A. Kikuchi*, Tohoku University, Japan, *H. Ota*, AIST, Japan, *P.-H. Su, Y. Li*, National Chiao Tung University, Taiwan, *S. Samukawa*, Tohoku University, AIST, Japan, ***Kazuhiko Endo***, AIST, Japan **INVITED**

Ge is a promising material for use as high mobility channel in future CMOS. For 5-nm-node CMOS and smaller, to attain electrostatic controllability of the gate electrode, a multichannel fin structure is utilized. Fin structure formation in Ge FinFETs on GeOI substrates is mainly performed by ICP etchings. However, ICP etching causes plasma induced damages owing to the ultraviolet (UV) light generated from the ICP and charge up by ionized atoms. A concern is that such etching damage reduces the performance and reliability of Ge-channel CMOS. In this work, to break-through these plasma induced damages, we demonstrated defect-free and highly anisotropic Ge etching for Ge FinFET fabricated by Cl neutral beam etching.

There are two advantages in the neutral beam etching process. 1) The wafer is not exposed by the UV light generated from the plasma through the high-aspect-ratio carbon aperture plate. 2) Ions are efficiently neutralized by collision with the carbon aperture plate. Thus, in neutral beam etching, the influences of the UV light and charge-up can be perfectly eliminated and defect-free etching can be realized.

In the ICP etching, the Ge fin is formed but has a trapezoidal shape. On the other hand, the Ge fin in the case of neutral beam etching can be vertically formed as compared with that in the case of the ICP etching. A channel surface with atomic-level smoothness was confirmed in neutral beam etching while some roughness was observed in the ICP etching. In neutral beam etching without UV light irradiation, the Ge surface is not damaged, and a surface dangling bond is formed only on the atomic layer and it undergoes a chemical reaction with the reactive species [1]. Thus, atomic layer etching can be realized by neutral beam etching.

The $|I_d|$–V_d and $|I_d|$–V_g characteristics of the Ge FinFET fabricated by neutral beam etching are markedly improved as compared with those of the FinFETs fabricated by ICP etching, in n- and p-type FinFETs. $g_{m\,max}$ for the Ge FinFET fabricated by neutral beam etching is two times higher for the nFinFET and 10% higher for the pFinFET than those of the FinFETs fabricated by ICP etching, regardless of the fin thickness. In the case of neutral beam etching, since there is no etching damage in the Ge fin, the interface state and surface roughness are drastically lowered. This is the reason for the improved $g_{m\,max}$ for the n- and p-type Ge FinFETs fabricated by neutral beam etching. Thus, the atomic-level flatness and damage-free etching in the Ge fin formation are essential to high performance Ge FinFETs, which can be realized by neutral beam etching.

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11:40am **PS+NS+SS+TF-ThM12 Numerical Simulations of Atomic-Layer Etching (ALE) for SiO_2 and SiN**, ***Yuki Okada***, Osaka University, Japan, *R. Sugano*, Hitachi, Ltd., Japan, *M. Isobe, T. Ito, H. Li, K. Karahashi, S. Hamaguchi*, Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer deposition (ALD) and atomic-layer etching (ALE), in which deposition or etching processes take place layer by layer with each step having self-limiting chemical reactions. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO2 and SiN based on digital or pulsed application of fluorocarbon or hydrofluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive species and low-energy incident ions are supplied to a SiO2 or SiN surface alternatively. A supply of a certain amount of chemically reactive species to the surface does not spontaneously induce etching reactions. However, when the surface with such reactive species is subject to ion bombardment, energy and momentum supplied to the surface by incident ions activate surface reactions and etching reactions take place. If the ion bombardment energy is sufficiently low, this etching process stops when reactive species are depleted from the surface. In this study, we have examined various combinations of reactive species and ion bombardment. For example, in the case of SiO2, reactive species and ions used in this study are fluorocarbon radicals and low-energy (e.g., 40 eV) Ar+ ions. In the case of SiN, reactive species and ions are hydrogen radicals and low-energy (e.g., 10 eV) Ar+ ions. Also in the case of SiN, we have used simultaneous injection of hydrogen radicals with low energy CF3+ ion bombardment as a radical supply process and low-energy (e.g., 50 eV) Ar+ ion injections as a process to remove excess fluorocarbon deposited on the surface. In the last case, etching self limit occurs because of accumulation of a fluorocarbon layer, rather than the removal of it. It has been found that, in most cases, the complete removal of reactive species from the surface is not easy and the control of remaining reactive species on the surface after each digital process step is the key for the success of ALE process development.

12:00pm **PS+NS+SS+TF-ThM13 Organometallic Etching Chemistry for Thermal Atomic Level Etching of Lanthanum Oxide**, ***Yoshihide Yamaguchi***, *K. Shinoda*, Hitachi, Japan, *Y. Kouzuma, S. Sakai, M. Izawa*, Hitachi High-Technologies Corp., Japan

The demand for thermal atomic level etching (ALEt) of a wide variety of materials including silicon-based materials, metals, and high-k materials is increasing as semiconductor device geometries continue to shrink. To meet the increased demand, remarkable progress into ALEt research has been made in the last few years. One example is the pioneering research on the thermal ALEt of hafnium oxide emerged [1], where hafnium oxide sequentially reacted with HF and a stannous organometallic compound (Sn(acac)2). Thermal ALEt of SiN is another example [2][3], where sequential reactions of a plasma-assisted self-limiting surface modification and a thermal desorption of the self-limiting layer was employed.

In this work, we present our challenge for the thermal ALEt of lanthanum oxide by using surface modification followed by thermal desorption. A key technology of this ALEt is the novel organometallic chemistry for the one-step surface modification of lanthanum oxide. A lanthanum oxide sample exposed to gas of fluorine-containing ketone together with a stabilizer led to the formation of volatile organic species on the sample surface, while a SiO2 sample remained unchanged under the same process condition. The gas-exposed lanthanum oxide sample was then annealed at elevated temperatures under vacuum to remove the volatile species from the surface. After these consecutive processes, the volatile organic species from the lanthanum oxide sample were collected and identified by nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy. These results indicated that the volatile species was an organo-lanthanum complex bearing the fluorine-containing ketone moiety as the ligand. On the basis of these results, a novel selective dry-chemical removal of lanthanum oxide was successfully demonstrated.

Several results on selective dry-chemical removal of lanthanum oxide with respect to TiN, metal oxide, and some other material will also be disclosed.

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Plasma Science and Technology Division
Room: 22 - Session PS-ThM

Plasma Sources
Moderators: Rebecca Anthony, Michigan State University, David Ruzic, University of Illinois at Urbana-Champaign

8:00am **PS-ThM1 New Plasma Source Generating High Radical Flux With Low Ion and Photon Flux**, *Y. Pilloux*, ***David Lishan***, *M. Segers*, Plasma-Therm LLC

Substrate cleaning of organics utilizes a range of technologies that includes wet processing, barrel ashers, and microwave driven downstream plasmas. In this work, we introduce a unique inductively coupled downstream source configuration to generate high density radical concentrations (>1.1E+17 cm^{-3}) but without high ion and photon fluxes typically found in conventional inductively coupled plasmas. Although the plasma discharge tubes are isolated from the treatment chamber, they deliver a large concentration of free radicals. The low ion and photon exposure significantly reduces the opportunity for damage to sensitive layers. This inductive plasma arrangement prevents local heating and charging on the wafer, and behaves similarly as a microwave downstream plasma. However, a higher oxygen radical flux promotes more efficient organic layer cleaning and/or removal of photoresists even when low thermal budgets are a constraint.

This work will first describe the High Density Radical Flux (HDRF) source and characterize its behavior in generating high radicals flow and low ions in local downstream, on the wafer surface. Second, several applications using the HDRF technology will be discussed. These applications will include cleaning of 30:1 aspect ratio (AR) silicon vias, removal of sacrificial layers in MEMS structures, low temperature photoresist removal, and surface smoothing of Bosch generated sidewalls using micro-isotropic etching. With a low local electrical potential, due to the limited ions present in the process chamber, the HDRF is particular efficient with 3D structures on the wafer (e.g. MEMS and other high AR features) where preventing ion shielding effects is important.

8:20am **PS-ThM2 Towards Plug-and-Play Tailored Voltage Waveform Plasma Sources: Progress in Matching and Calibration**, ***Erik V. Johnson***, LPICM, Ecole Polytechnique, France, *K. Yamaki*, LPP-CNRS, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France

The use of non-sinusoidal Tailored Voltage Waveforms (TVWs) to excite a plasma process has proven to be a rich field. Performing deposition or etching using such TVWs been shown to provide (1) a greater degree of control over outcomes, (2) more understanding of those processes, and even (3) processes unachievable by any other means, such as electrode-selective deposition.

The dream design for a Tailored Voltage Waveform plasma source is one that can ensure that an exact version of a given waveform appears on the RF electrode, but without increasing the complexity and cost of the source far beyond that of a single frequency RF source (including matchbox). These requirements are challenging due to the multi-harmonic nature of TVW's; the matching network must simultaneously provide efficient impedance matching at multiple frequencies, and as the phase between harmonics matters, for certain systems the waveform appearing at the RF feedthrough will not be a scaled version of the one on the electrode.

We address these two challenges directly. For the multi-frequency impedance matching challenge, we present progress on the design and fabrication of a high-power multi-frequency matchbox. This system allows the semi-independent tuning of the matching condition at each harmonic. For the second challenge involving uncertainty in the waveform appearing at the electrode, we present results using the plasma properties themselves to eliminate potential sources of error in the waveform. This technique avoids the need for probes located within the vacuum chamber, optical access to the plasma, or limiting the waveforms to lower frequencies.

8:40am **PS-ThM3 Selective Radical Production in Remote Plasma Sources**, ***Shuo Huang***, University of Michigan, *V. Volynets*, *S. Lee*, *S. Nam*, *S. Lu*, Samsung Electronics Co. Ltd., Republic of Korea, *M.J. Kushner*, University of Michigan

Remote plasma sources (RPS) are being used to achieve isotropic etching with high selectivity by avoiding charging, energetic ion bombardment and UV/VUV radiation using long distance and discriminating barriers between the RPS and the substrate. By using multiple plasma sources or multiple gas inlets at different locations, the reaction pathway can be optimized for producing desirable process radicals. NF_3 and HBr are frequently used sources of F and Br atoms, the main etchants of silicon-containing materials, by electron impact dissociative attachment and excitation. NF_x ($x = 1 – 3$) and HBr can exothermically react with other neutral species to produce F, Br and OH radicals, which also enables customizing the reaction pathway by flowing gases downstream of the RPS.

In this paper, we report on results from a computational investigation of an inductively coupled RPS having multiple gas inlets with the goal of determining strategies for selectively producing reactive fluxes. The investigation was performed using the plug flow mode of 0-dimensional model, Global_Kin and in 2-dimensions using the Hybrid Plasma Equipment Model (HPEM). With $NF_3/N_2/O_2$ mixtures flowed through the RPS from an upstream inlet, the dominant radicals flowing downstream are F and O formed through dissociative excitation and attachment of NF_3 and O_2. NO molecules were formed through endothermic reactions among N_2, N, O_2 and O species. With HBr injected downstream of the plasma source, mixing with the plasma produced radicals enable another level of selectivity. Due to lack of electrons and low gas temperature (~ 350 K) downstream, HBr reacts with F and O through exothermic reactions (HBr + F > HF + Br, HBr + O > OH + Br and HBr + OH > H_2O + Br) and the dominant downstream radicals transition from F and O to Br and HF. Vibrationally excited HF(v), a highly polar molecule, may be formed through reactions having a larger exothermicity than the vibrational quanta, and so may produce a significant flux of activation energy to the wafer

Work was supported by Samsung Electronics, DOE Office of Fusion Energy Science and the National Science Foundation.

9:00am **PS-ThM4 On Electron Heating in Magnetron Sputtering Discharges**, ***Jon Tomas Gudmundsson***, University of Iceland, *D. Lundin*, Université Paris-Sud, France, *M.A. Raadu*, KTH-Royal Institute of Technology, Sweden, *T.M. Minea*, Université Paris-Sud, France, *N. Brenning*, KTH-Royal Institute of Technology, Sweden

The magnetron sputtering discharge has been applied successfully in various industrial functions for over four decades. Sustaining a plasma in a magnetron sputtering discharge requires energy transfer to the plasma electrons. In the past, the magnetron sputtering discharge has been assumed to be maintained by cathode sheath acceleration of secondary electrons emitted from the target, upon ion impact. These highly energetic electrons then either ionize the atoms of the working gas directly or transfer energy to the local lower energy electron population that subsequently ionizes the working gas atoms. This is the essence of the well-known Thornton equation, which in its original form [1] is formulated to give the minimum required voltage to sustain the discharge. However, recently we have demonstrated that Ohmic heating of electrons outside the cathode sheath is typically of the same order as heating due to acceleration across the sheath in dc magnetron sputtering (dcMS) discharges [2]. The secondary electron emission yield γ_{see} is identified as the key parameter determining the relative importance of the two processes. In the case of dcMS Ohmic heating is found to be more important than sheath acceleration for secondary electron emission yields below around 0.1. For the high power impulse magnetron sputtering (HiPIMS) discharge we find that direct Ohmic heating of the plasma electrons is found to dominate over sheath acceleration by typically an order of magnitude, or in the range of 87 – 99 % of the total electron heating. A potential drop of roughly 80 - 150 V, or 15 - 25% of the discharge voltage, always falls across the plasma outside the cathode sheath [3]. We also discuss the influence of the magnetic field strength on the discharge properties.

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9:20am **PS-ThM5 High-Density Plasma Generation in Low-Pressure Metamaterial Space**, ***Osamu Sakai***, The University of Shiga Prefecture, Japan **INVITED**

Generation of high-density plasmas have been one of the main topics in science and technology of low-temperature plasma since high throughputs in material processing such as dry etching and thin-film deposition are achieved by high electron density which enhances chemical and physical processes in weakly-ionized plasma. When we use microwaves in plasma generation, there have been several methods proposed so far for high-density plasma, like electron-cyclotron-resonance plasma and surface-wave plasma.

Here we propose another scheme in which a magnetic metamaterial makes magnetic permeability in discharge space negative. Microwave propagation in simple discharge space with no objects and no external magnetic field is limited by cutoff density where electric permittivity or dielectric constant is down to zero. When magnetic metamaterial who has negative permeability is installed in the space, microwave propagation is possible beyond the cutoff density, with negative refractive index state with negative permittivity that indicates high electron density. Experimental observation confirmed existence of this scheme, and electron density was much higher than the cutoff density (approximately $7x10^{10}$ cm^{-3} when microwave frequency is 2.45

GHz) [1]. The value of electron density has no limitation with smooth microwave propagation with large negative values of refractive index.

In addition to these advantages on generation of high-electron-density plasma, recent experimental studies have revealed that this scheme of plasma generation has roles of high energy storage and an efficient energy converter. From the estimations based on monitored electron density and temperature, the existing energy density in the plasma generation space with the metamaterial is by 3 orders of magnitude larger than that in microwave propagation in the free space. Such stored energy is efficiently converted into the second harmonic wave via nonlinear and asymmetry effects between plasma and metamaterial [2], as well as into chemical energy via enhanced dissociation of gas molecules. These facts indicate that this plasma source will contribute to novel functions that can be hardly established using other plasma generation schemes as well as the general function as a high-density plasma source for material processing.

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11:00am **PS-ThM10 Optical Emission Spectroscopy of a Spark-coupled Laser Aluminum Plasma for Multicharged Ion Generation**, ***Md Mahmudur Rahman***, *O. Balki, M. Shaim, H.E. Ali*, Old Dominion University

A spark-coupled laser plasma is used to generate multicharged ions. A Q-switched Nd:YAG laser (λ = 1064 nm, , τ = 8 ns, pulse energy ≤ 100 mJ, repetition rate 1 Hz) ablates an aluminum target creating a laser ion source, while the spark discharge further enhances ion generation. A high-voltage pulse-forming network produces up to 12 kV, ~1 µs pulse across the spark electrodes. Line emission from neutrals and ions are probed by optical emission spectroscopy. These spectral lines are used to obtain time-integrated, spatially-resolved electron temperature (T_e) from the Boltzmann plot and electron density (n_e) from Stark broadening. The pulse forming network is triggered with a thyratron through a delay in order to optimize the timing between the laser pulse and the spark discharge for best spark energy coupling to the laser plasma. A delay of 100 ns is found to produce the best coupling of the spark energy to the laser plasma. For a spark energy of 1.5 J, the intensity of the Al IV 372.6 nm and Al III 361.2 nm lines increases by a factor of ~10 and ~ 6, respectively compared to that from the laser plasma alone. The effective ion temperature (T_{ieff}) associated with translational motion along the plume axis is calculated from the ion time-of-flight (TOF) signal and compared with T_e. The results show that T_{ieff} is much larger than T_e, although the plasma is considered to be in local thermodynamic equilibrium. This result is explained in view of the different regions of the plasma probed by ion TOF and optical spectroscopy.

11:40am **PS-ThM12 Effect of Secondary Electrons on the Ionization Dynamics and Control of Ion Properties in Electronegative Capacitive Discharges**, ***Aranka Derzsi***, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary **INVITED**

The realization of the separate control of the ion flux and ion energy distribution at the substrate in capacitively coupled radio frequency (RF) discharges is an important issue for various applications of plasma processing, ranging from plasma based etching and deposition procedures in the semiconductor industry to plasma assisted surface treatment of medical interest. In order to attain such independent control of the ion properties, the application of non-sinusoidal voltage waveforms (pulse-like, or saw-tooth-type, for instance), known as „tailored“ or „customized“ RF voltage waveforms for the excitation of capacitive RF discharges, has recently been introduced. Such waveforms differ from the conventionally applied sinusoidal voltages by exhibiting different absolute values of their positive and negative extrema. This control method is based on the electrically asymmetric plasma response, known as the Electrical Asymmtery Effect, observed when non-sinusoidal exciting voltage waveforms are applied, leading to the generation of a dc self-bias voltage in a geometrically symmetric discharge cell. The applications of tailored voltage waveforms, generated by using multiple harmonics of a base frequency (multi-frequency excitation), offer new possibilities for controlling plasma properties. Most of the systematic studies on capacitive RF plasmas excited by tailored voltage waveforms have been conducted so far in electropositive capacitive RF discharges. However, the applications usually require complex mixtures of reactive gases. For instance, oxygen is widely used in etching and thin film deposition techniques, CF_4 is also frequently applied to etch silicon and silicon-dioxide in microelectronics.

Secondary electrons generated at the electrodes are known to influence the ionization dynamics and induce transitions of the discharge operation mode from the α-mode to the γ-mode in electropositive discharges at high driving voltage amplitudes and/or pressures. In electropositive discharges these γ-electrons influence the quality of the separate control of ion properties. Here, we report our systematic simulation studies of the effect of secondary electrons on the electron power absorption and ionization dynamics and on the quality of the separate control of ion properties at the electrodes in low-pressure capacitively coupled RF discharges operated in reactive, electronegative gases excited by tailored voltage waveforms.

Advanced Surface Engineering Division
Room: 11 - Session SE+PS+SS-ThM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Suneel Kodambaka, University of California at Los Angeles

8:00am **SE+PS+SS-ThM1 Key Features of Reactive High Power Impulse Magnetron Sputtering**, ***Daniel Lundin***, CNRS/Paris-Sud University, France **INVITED**

For many thin film applications, such as optical coatings, energy-related coatings, hard coatings, etc., the coated layers are not single metal thin films, but rather compound coatings obtained from at least one metal (e.g. Al, Ti) or a non-metal (e.g. C, B) and a reactive gas (e.g. O_2, N_2). This talk will address the challenges and possibilities of depositing compound coatings using a promising thin film deposition technology called high power impulse magnetron sputtering (HiPIMS), and how this method differs from conventional processes. Both nitride and oxide systems will be covered during different modes of operation including pure argon, metallic, transition, and compound modes. Key features in reactive HiPIMS, such as eliminated/reduced hysteresis, stable high-rate deposition in the transition mode, and self-sputter recycling versus working gas recycling, will be addressed by using results from recent plasma process modelling in combination with experimental plasma characterization. Ionization of the material flux will be discussed in detail, since it enables effective surface modification via ion etching and self-ion assistance during film growth, as well as being a key feature in HiPIMS. This includes exploring the temporal evolution of the discharge plasma parameters, such as electron density and temperature, the neutral and ion composition, the ionization fraction of the sputtered vapor as well as of the reactive gas mixture, and the composition of the discharge current. The focus will be on identifying dominating physical and chemical reactions in the plasma and on the surfaces of the reactor affecting the plasma chemistry.

8:40am **SE+PS+SS-ThM3 Depositions of Al_2O_3 Coatings by HiPIMS via Closed-loop Control using a Plasma Emission Monitoring Sensor**, ***Jianliang Lin***, *R. Wei, K. Coulter*, Southwest Research Institute, *F. Papa*, Gencoa Ltd.

Reactive sputtering of insulating oxide coatings, e.g. alumina (Al_2O_3),by high power impulse magnetron sputtering (HiPIMS) is of great interest, as the increased target ionization in HiPIMS can be used for improving the structure and properties of the coatings. Typically there are two challenges for the process including arc suppression and overcoming the decreased deposition rate due to target poisoning. In this paper, Al_2O_3 coatings were reactively sputtered by HiPIMS with deep oscillatory pulses using closed-loop control of oxygen partial pressure to achieve high deposition rates. Stable and Arc-free deposition processes were obtained with a peak target current density up to 1.2 Acm^{-2} by optimizing key pulsing parameters of deep oscillating pulses. The closed-loop control was achieved by controlling oxygen partial pressure from a remote plasma emission monitoring (PEM) sensor which ionizes sample plasma away from the deposition zone. The deposition rate, microstructure and properties of the Al_2O_3 coatings deposited at different oxygen partial pressures and HiPIMS peak target current densities were investigated and compared to those obtained by traditional pulsed dc.

9:00am **SE+PS+SS-ThM4 The Influence of Spokes on Spatial and Energy Distributions of Ions in Magnetron Sputtering Discharges**, ***Matjaz Panjan***, Jozef Stefan Institute, Slovenia, *K. Tanaka, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory

The formation of dense plasma structures, called ionization zones or spokes, is now a well documented phenomenon in magnetron discharges [1,2]. Experiments and models suggest that these structures strongly influence the transport and the energy of electrons and ions [3,4]. Previously, we measured ion energy distribution functions in the plane of the magnetron by moving its target surface sideways with respect to the orifice of a combined mass spectrometer and energy analyzer (EQP300, Hiden Ltd.) [5]. The measurements showed asymmetric flux of ions in the plane of the target, which was attributed to the moving spokes. Here we report on the measurements of ion energy distribution functions for two different magnetron-EQP arrangements. In the first experimental arrangement, the

orifice of EQP300 was directed in the plane of the magnetron and the magnetron was moved in the axial direction. In the second arrangement, the magnetron was rotated around its center for different polar angles while the distance between the target and the orifice was fixed. Measurements were performed in direct current magnetron sputtering (DCMS) using a 3" magnetron and niobium target. Ion energy distribution functions were measured for single and double charged argon and niobium ions. The first experiment showed that the largest flux of high-energy ions (i.e. ions above 10 eV) exists around 30 mm above the target. Overall, higher fluxes were observed in the **E×B** direction than in the **-E×B** direction. Polar measurements showed larger ion fluxes and higher ion energies near the target plane as compared to considerably lower fluxes and energies perpendicular to the target. The results of the measurements are discussed with respect to the plasma potential structure and associated electric field distribution of a rotating spoke, which we recently measured in DCMS discharge [6].

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9:20am **SE+PS+SS-ThM5 Silicon Nitride Deposition for Organic Electronics by VHF (162MHz)- PECVD**, *G.Y. Yeom*, ***KiHyun Kim***, *K.S. Kim, Y.J. Ji, J.S. Oh*, Sungkyunkwan University, Republic of Korea

Deposition of permeation barrier film for organic-based electronics is one of the most important issues in organic electronic device fabrication process because the permeation of moisture and oxygen into organic materials causes significant degradation of the device performance and stability. In this study, as an effective thin film barrier material for organic electronics, we investigated low-temperature (~ 80 °C) silicon nitride deposited by very high frequency (VHF, 162MHz) PECVD using multi-tile push-pull electrodes with a gas mixture of NH_3/SiH_4. The composition of the silicon nitride film deposited by VHF PECVD was similar to the ideal stoichiometry of silicon nitride (Si : N = 1 : 1.33) and the deposited film exhibited high optical transparency over 90% in the visible region. The deposited silicon nitride also exhibited a high step coverage of 1:1.29. When water vapor transmission rate (WVTR) was measured with single (400 nm thick) SiN_x layer deposited on PET, excellent WVTR of 4.39 x 10^{-4} g/m^2·day could be obtained. I-V characteristics of organic light emitting diode (OLED) devices were measured before and after the film deposition on the devices, and no noticeable changes of I-V characteristics after the deposition of silicon nitride film on the OLED devices were observed indicating no noticeable electrical damage by the deposition of silicon nitride using VHF PECVD which is ascribed by low electron temperature characteristics of the plasma and the lack of current flow to the substrate for the VHF-PECVD method utilizing multi-tile push-pull-type electrodes.

Keywords : encapsulation, silicon nitride, organic light emitting diode (OLED), very high frequency (VHF), water vapor transmission rate (WVTR), step coverage

9:40am **SE+PS+SS-ThM6 Printed Circuit Board Assembly- an Ensemble of Different Surface Energy Components and their Surface Modification**, ***Shailendra Vikram Singh***, *S. Woollard, G. Aresta, A.S. Brooks, G. Hennighan*, R&D Semblant Limited

Plasma-produced thin film liquid ingress barrier coatings for electronic devices have several advantages over conventional parylene-based coatings. However, issues connected with plasma processing conditions, electronic device casing designs, and manufacturing technicalities and throughput, independently or in combination, may limit appropriate implementation of such coatings. Hence, it is critical to apply such coatings directly on the printed circuit board assembly (PCBA) of a device to achieve excellent protection against liquid ingress damages. Moreover, an additional coating on the device case can provide extra features and advantage. A PCBA is a complicated substrate in terms of conformality and adhesion requirements. It comprises an ensemble of different surfaces of different shapes and sizes and various materials: metals, polymers, polyester (fiber and resins), graphite, solder residue, etc. The surface energies of these components on boards vary from ~10 mN/m to up-to ~70 mN/m. In this study, we have addressed the surface treatment and etch cleaning requirements for better adhesion of a reworkable conformal plasma coating. The main challenge resides in altering the surface energy consistently across all the surfaces present on a PCBA. Furthermore, in a manufacturing situation the chance of surface contamination due to handling is very high. Especially, in our case, where, the manufacturing speed is >700 standard phone PCBAs/hr/coater batch. Surface chemistry, type and amount of such randomly introduced contaminations cannot be easily predicted. In this regard, we have also studied several hypothetical contamination situations investigating the relationship between etch-clean and surface energy change.

11:00am **SE+PS+SS-ThM10 Plasma Surface Engineering of Biomaterials**, ***Paul K. Chu***, City University of Hong Kong, Hong Kong **INVITED**

The chemical and biological interactions between biomaterials and biological tissues depend on the surface properties of the biomaterials and associated biological responses. However, many types of biomaterials that possess favorable bulk properties such as hardness, strength, robustness may not perform the pre-designed biological functions and so surface modification is frequently performed to enhance the biological and chemical properties. Plasma-based technology offers the unique capability that selected surface properties can be modified to address specific biological requirements while the desirable bulk properties of the materials such as those mentioned above are preserved. In particular, plasma immersion ion implantation and deposition (PIII&D) is one of the widely used plasma-based surface techniques suitable for biomaterials and biomedical devices. Being a non-line-of-sight technique, it is especially suitable for biomedical devices with a complex shape like dental and orthopedic implants, scoliosis correction rods, cardiovascular stents, and artificial heart valves. In this invited presentation, recent research performed in the Plasma Laboratory of City University of Hong Kong related to plasma treatment of biomaterials and biomedical devices will be described. Examples include biocompatibility of nanostructured surfaces and coatings, biocompatibility of biodegradable materials, bacterial resistance, as well as osseointegration and osteogenesis.

12:00pm **SE+PS+SS-ThM13 Tuning the Properties of Plasma Polymer Varying the Substrate Temperature: a Step Toward the Fabrication of Micro/nano Pattern**, ***Damien Thiry***, University of Mons, Belgium, *N. Vinx, F.J. Aparicio*, University of Mons, *T. Godfroid, S. Deprez*, Materia Nova, *R. Snyders*, University of Mons, Belgium

Plasma polymerization is a well-known technique developed during the last decades for the development of solid organic functionalized thin films (100nm - 1µm) from a large range of organic precursors. The retention of the precursor functionalities and the synthesis of soft material has rapidly become a challenge in the field. The usual strategy consists in limiting the fragmentation of the precursor in the plasma by reducing the load of energy in the discharge. In this work, an almost unexplored approach based on varying the substrate temperature for a given set of plasma parameters is studied in order to extend the control that plasma polymerization provides over the cross-linking degree and the chemical composition of the formed layers. As a case study, propanethiol plasma polymer films (Pr-PPF) finding application as support for gold nanoparticles and biomolecules immobilization are investigated.

The deposition rate of Pr-PPF was found to follow an Arrhenius law with the substrate temperature (T_s) varying from -10 °C to 45°C. This behavior is explained through the influence of T_s on the residence time of the film-forming species at the growing film interface. With regard to the chemical composition of the layers, the atomic sulfur content is nearly constant (i.e. ~ 45 at. %) in the range -10 °C < T_s < 23 °C and strongly decreases (i.e. ~ 30 at. %) for T_s > 23 °C. Based on these data, it can be proposed that a critical T_S has to be reached for favouring the desorption of sulfur-based species before their incorporation within nascent plasma polymer. On the other hand, "rough" indentations measurements combined with optical microscopy imaging reveal that for T_s < 10°C, a deformation of the Pr-PPF takes place when applying a force (i.e. 1 mg) on the top of the polymer with the tip of the profilometer. Furthermore, a fast recovery of the plasma polymer layer occurs over a time scale of about 3 min. As an important result, these data disclose the possibility to produce soft and visco-elastic plasma polymer layer. Finally, inspired by the wrinkling phenomenon occurring in a bilayer system exhibiting a high contrast in terms of mechanical properties, a thin aluminium coating is deposited by magnetron sputtering on the top of a low cross-linked Pr-PPF synthesized at T_s = 10°C. The mismatch between the mechanical properties between both layers results in the formation of a wrinkled surface. By tuning the thickness of the aluminium and the Pr-PPF coatings, the height (i.e. from 0.4 to 5.2 µm) and the width (i.e. from 0.6 µm to 6.5 µm) of the nano/micro objects can be easily tailored offering a great flexibility in terms of nano/micro engineering.

Plasma Science and Technology Division
Room: 23 - Session PS+TF-ThA

Plasma Enhanced ALD

Moderators: Steven George, University of Colorado at Boulder, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+TF-ThA1 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of Vanadium Nitride using Tetrakis(Dimethylamido)Vanadium and Nitrogen Plasma**, ***Mark Sowa***, Ultratech, Inc., *L. Ju, N.C. Strandwitz*, Lehigh University, *A.C. Kozen*, US Naval Research Laboratory, *G. Zeng, B.A. Krick*, Lehigh University

Vanadium nitride (VN) has been proposed for a variety of thin film electronics applications including interconnect diffusion barrier and supercapacitor electrodes. As with other transition metal nitrides, VN exhibits excellent mechanical properties and has been studied for its self-lubricating coating performance. VN thin films have been created primarily through PVD methods. Recently, atomic layer deposition of VN has been reported with tetrakis(diethylamido)vanadium (TDEAV) with NH_3 gas and tetrakis(ethylmethylamino)vanadium (TEMAV) with NH_3 gas and NH_3 plasma.

We report plasma enhanced atomic layer deposition results for VN using tetrakis(dimethylamido)vanadium (TDMAV) with N_2 plasma. Optimized TDMAV pulsing and N_2 plasma conditions have been established. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties). Depositions were investigated over 150 - 300 °C. Sub-100 μΩ-cm resistivities have been realized at 300 °C.

2:40pm **PS+TF-ThA2 Optimizing Process Parameters for Plasma Assisted Atomic Layer Deposition**, ***David Boris***, *V.D. Wheeler*, Naval Research Laboratory, *V.R. Anderson*, ASEE (residing at NRL), *N. Nepal*, Naval Research Laboratory, *S.G. Rosenberg*, ASEE Postdoctoral Fellow, *A.C. Kozen*, ASEE (residing at NRL), *J.K. Hite, S.G. Walton*, Naval Research Laboratory, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ optical emission spectroscopy and charged particle collectors to characterize a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PA-ALD of AlN and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.

3:00pm **PS+TF-ThA3 Tuning of Optical and Structural Properties of ZnO Deposited by Room Temperature-plasma Assisted Atomic Layer deposition**, ***Alberto Perrotta***, *J. Pilz, A.M. Coclite*, Graz University of Technology, Austria

Wurtzite-structured ZnO thin films have been extensively investigated because of their unique optical, electrical, and piezoelectric properties, making it the material of choice in various applications such as transparent conducting electrodes, surface acoustic wave devices, and as sensors. In engineering ZnO-based devices, the material characteristics have to meet specific requirements in terms of opto-chemical and electrical properties and crystalline structure, together with very high conformality and thickness control. Plasma-assisted atomic layer deposition (PA-ALD) has been shown able to deposit very high quality ZnO thin films, combining the low process temperature with the exceptional atomic-thickness control. Furthermore, the properties of the material can be tuned by varying the plasma characteristics, making it suitable to adapt the material to specific applications.

In this contribution, high quality ZnO thin films have been deposited by PA-ALD optimized at room temperature, adopting diethyl zinc (DEZ) and oxygen plasma. The properties of the material have been investigated as a function of the radio frequency plasma power and plasma exposure time, and characterized by X-ray diffraction (XRD), gracing incidence XRD with synchrotron radiation, spectroscopic ellipsometry (SE), and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction patterns of polycrystalline ZnO thin films showed rather preferred (100) orientation and XPS analysis showed the complete removal of the DEZ carbon ligands, confirming the possibility to obtain high quality crystalline ZnO at room temperature. Furthermore, the effect of the plasma power on the opto-chemical properties, growth, and crystalline structure has been investigated. Finely tuning of the optical properties of the PA-ALD ZnO layers has been achieved, with refractive index ranging between 1.82 and 1.89 at 633 nm. Moreover, the absorption has been found to increase and shift in the visible range at low plasma power. In addition, XRD showed a distortion of the (100) peak at low and high plasma power, indicating the possibility to vary the crystallite size as a function of the plasma parameters.

As an outlook, the optimized PA-ALD process at room temperature allows the deposition of ZnO on thermo-sensitive nanostructured templates, inferring the possibility to adopt it in engineering (flexible) structured devices.

3:20pm **PS+TF-ThA4 Influence of Plasma Power on the Si Solar Cell Passivation Properties of Al_2O_3 Thin Films deposited by Atomic Layer Deposition at 90 °C**, *Z. Zhu*, Beneq Oy, Finland, *P. Sippola*, Aalto University, Finland, ***Emma Salmi***, Beneq Oy, Finland

In the recent years ALD Al_2O_3 surface passivation for Si solar cells has gained increasing popularity. The excellent passivation properties of ALD Al_2O_3 are based on a combined effect of chemical passivation and fixed high negative charge density. A bulk of the work has concentrated on thermal ALD, but also plasma enhanced ALD (PEALD) has been considered. However, the effect of plasma parameters, particularly plasma power, on the passivation properties remain uncharted.

In this work, we have studied the effect of plasma power on the properties of PEALD Al_2O_3 deposited at low temperatures with focus on the Si solar cell passivation. The Al_2O_3 was grown from TMA and O_2 plasma. All depositions were done with a Beneq TFS 200 ALD reactor at 90 °C. The lifetime was studied for as deposited and post-annealed samples.

The plasma power significantly affected the film properties. Low plasma power appeared to lead to the lowest film quality in regards of purity, density and refractive index. When the power was increased from 50 to 100–300 W the density increased from 2.6 to 2.8 g/cm^{-3}. Similarly, the refractive index increased from 1.61 to 1.62 (at 628 nm). The higher plasma power appeared to increase the amount of available O radicals, leading to more efficient reaction completion and improved film optical and structural properties. The same trend was also clear for the passivation properties for Si solar cells. For a 25 nm Al_2O_3 deposited with 50 W plasma power and annealed at 400 °C the lifetime at 10^{15} cm^{-3} injection level was 1.1 ms, while for Al_2O_3 deposited with 100 or 180 W it was 2.0 ms. The interface properties were also influenced. The 50 W sample had the lowest density of negative charge and the highest interface defect density, which agreed with the lower lifetime of the sample. Interestingly, the 100 W sample had the lowest level of defect density. This can be related to the more moderate level of ultraviolet radiation from the O_2 plasma that the 100 W sample was exposed to as compared to the 180 W sample. Nevertheless, the 180 W sample had the best passivation properties due to its highest negative charge density. In fact, the negative charge density plays a major role in surface passivation when the magnitude of the negative charge density is much greater than that of the defect density.

High quality surface passivation of Si solar cells was achieved with PEALD Al_2O_3 grown at 90 °C. The passivation properties were shown to significantly improve with increasing plasma power.

4:00pm **PS+TF-ThA6 Optimizing MoO_3 Plasma-enhanced ALD Thin Films for use in Controllable 2D Material Synthesis**, ***Brittney Burant***, MIT Lincoln Laboratory

Monolayer MoS_2 is a direct bandgap semiconductor with promising properties for novel devices. It has been shown that valley polarization can be achieved in MoS_2 monolayers with circularly polarized light, which would allow the realization of novel information processing architectures through manipulation of the valley pseudo-spin. However, current production methods of MoS_2 monolayers are either low yielding, or of relatively poor quality for valleytronic applications. To control the layer number, defectivity, and crystallinity of MoS_2, a novel method for limiting growth through the sulfurization of wafer-scale MoO_3 thin films has been developed.

Thorough characterization of the MoO_3 plasma-enhanced ALD process was performed to understand the effect of MoO_3 process parameters on the resultant MoS_2. MoO_3 films of 20-35 nm were deposited utilizing $(NtBu)_2(NMe_2)_2Mo$ as the organometallic precursor and O_2 plasma for the oxygen source. Variations in Mo precursor dose time and O_2 plasma exposure time show the expected trends, but substrate temperature effects are more significant. Growth per cycle increases with substrate temperature, from 0.88 Å/cycle at 100 ºC, to 1.32 Å/cycle at 350 ºC, with the highest GPC of 1.4 Å/cycle at 300 ºC. Raman spectroscopy shows that films grown at low temperature are amorphous, while polycrystalline film growth occurs above 250 ºC. These results are consistent with previously demonstrated MoO_3 growth utilizing the same process and precursor[1]. Surface roughness, as measured by AFM, also increases with temperature, which is consistent with a transition to polycrystalline film growth. Through XPS analysis, the deposited films were determined to be sub-stoichiometric in all deposits, averaging an O/Mo ratio of 2.6, regardless of substrate temperature.

MoS_2 films were grown on bare sapphire wafers by placing MoO_3 source wafers face-to-face with growth wafers. The wafers were oriented horizontally and enclosed in a graphite susceptor to enable inductive heating. Spacing between the MoO_3 source wafer and sapphire growth wafer was varied from 0 to 1 mm, and wafers were reacted at 700 ºC in H_2S gas. Initial reactions have shown increasing film deposition with decreased spacing between growth and source wafers. These results suggest that MoS_2 film growth by this method is vapor-phase transport limited. XPS data confirms the formation of MoS_2 on the growth wafer, however several layers of growth are observed. The effect of MoO_3 source wafer crystallinity on MoS_2 film quality is under investigation and will be presented.

[1] Vos, M., Macco, B., Thissen, N., Bol, A., Kessels, W. *JVST A*, **2015**, 34(1), 01A103-1-7.

4:20pm **PS+TF-ThA7 Plasma ALD of Fluorides: Process Characterization and *In Situ* Study of AlF_3 ALD**, ***Harm Knoops***, Oxford Instruments Plasma Technology, UK, *M.F.J. Vos, W.M.M. Kessels, A.J.M. Mackus*, Eindhoven University of Technology, The Netherlands

In this work we used TMA ($AlMe_3$) and SF_6 plasma for atomic layer deposition (ALD) of aluminum fluoride (AlF_3) films. SF_6 plasma is a novel co-reactant for ALD and we employed quadruple mass spectrometry (QMS) and optical emission spectroscopy (OES) to study the film growth. AlF_3 as well as other metal fluorides such as MgF_2 and CaF_2 generally have a wide bandgap (>10eV) and low refractive index (1.3-1.6). Due to these interesting properties they find use in many applications, including passivation layers in Li-ion batteries, electron transport layers in photovoltaics and protective coatings for optical devices. Previously, ALD of fluorides has been demonstrated using TiF_4 and TaF_5 as the fluorine source for the deposition of MgF_2, CaF_2 and LaF_3 and more recently using HF for AlF_3, ZrF_4, MnF_2, HfF_2, MgF_2 and ZnF_2.[1,2] The novel approach of using SF_6 plasma as a fluorine source is a promising alternative to HF, because of the ease of handling that SF_6 offers. Furthermore, SF_6 plasma provides increased reactivity at lower temperatures and allows for reduced purge times, similar to the benefits of using an O_2 plasma instead of H_2O for metal oxide ALD.

AlF_3 films were prepared on Si samples over a temperature window of 50°C to 300°C. Since SF_6 plasma etches Si and SiO_2, a thin Al_2O_3 layer was deposited prior to AlF_3 growth. Using *in situ* spectroscopic ellipsometry (SE) the growth per cycle (GPC) was determined to decrease from 1.5Å at 50°C to 0.5Å at 300°C. Interestingly, no significant impurity levels of S, C and O were detected in the bulk of the AlF_3 films using X-ray photo-electron spectroscopy (XPS), even for low deposition temperatures. Furthermore, XPS measurements showed a F/Al ratio of 3.0±0.2. The low impurity content and the stoichiometric F/Al ratio are in line with a refractive index of 1.35 at 633nm as determined by SE.

The reaction mechanism of the ALD process was addressed based on a combination of OES and QMS. These measurements suggest that CH_4 is released during the TMA dosing, and that CH_4, C_2H_2, HF, and CH_xF_y–species are formed during the plasma exposure. Furthermore, the reaction products during the plasma exposure show different trends in their release (e.g., mostly directly after striking the plasma or peaking after a few seconds of plasma exposure), which will be used to suggest a possible reaction mechanism. In addition, consumption of F can be observed similar to what is found in etching using SF_6 plasma. Overall this work shows that SF_6 plasma is a promising co-reactant which can inspire the ALD of a wide range of metal fluorides.

[1]Pilvi *et al.*, Chem. Mater. **20** (2008)

[2]Lee *et al.*, Chem. Mater. **28** (2016)

4:40pm **PS+TF-ThA8 Ion Energy Control During Remote Plasma ALD for Tuning Material Properties of Transition Metal Nitrides**, ***Tahsin Faraz***, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops*, Oxford Instruments Plasma Technology, UK, *S. Karwal, M.A. Verheijen, A.A. van Helvoirt*, Eindhoven University of Technology, Netherlands, *D.M. Hausmann, J. Henri*, Lam Research Corporation, *M. Creatore, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, it has been shown that the ion energy can play a significant role on the physical and chemical properties of thin films grown using plasma-enhanced atomic layer deposition (PEALD).[1] In this work, we demonstrate the impact of ion energy control during PEALD of transition metal nitrides (e.g., TiN_x, HfN_x, etc.) which are of great interest for nanoelectronic device applications owing to their low electrical resistivity and excellent diffusion barrier properties.[2] Ion energy control during plasma exposure was carried out in a commercial 200 mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with radio-frequency (RF) substrate biasing (13.56 MHz, up to 100 W power, -350 V resulting DC bias voltage). In such low pressure, remote inductively-coupled-plasma reactors, the ion energy can be controlled independently of the ion flux by applying an RF bias signal on the substrate table during the plasma exposure step.

Depositions performed under no bias conditions for TiN_x (at 200°C) and HfN_x (at 450°C) films using a 10 s H_2 (+Ar) plasma yielded electrical resistivities of 1960±60 and (900±0.7)x10^3 μΩcm and mass densities of 3.8±0.2 and 10.1±0.2 g/cm^3, respectively. Enhancing ion energies with substrate biasing during PEALD was observed to have pronounced effects on the chemical composition, microstructure and material properties of these transition metal nitrides. Energetic ion bombardment through application of bias voltages lowered film resistivity by one order of magnitude for TiN_x (139±10 μΩcm at -187V bias) and by two orders of magnitude for HfN_x ((330±70)x10^1 μΩcm at -130V bias) while also increasing their respective mass densities (4.9±0.2 and 10.5±0.2 g/cm^3). The residual stress of these films were also observed to change from tensile under no bias to compressive under bias conditions. The oxygen impurity content for films deposited without substrate biasing (~20 to 30%) was observed to be significantly reduced (≤ 4%) in films grown with bias voltages applied during plasma exposure. Furthermore, it will be discussed how the use of substrate biasing enhances PEALD process capability by providing several additional knobs (magnitude, duration and duty-cycle of bias, etc.) for tuning a wide range of material properties.

[1] Profijt et al., *J. Vac. Sci. Technol. A*, **31**, 01A106 (2013)

[2] Karwal et al., *J. Vac. Sci. Technol. A*, **35**, 01B129 (2017)

5:00pm **PS+TF-ThA9 Understanding the Challenges in Atomic Layer Deposition of SiN_x through Identification of the Surface Reaction Mechanisms**, ***Rafaiel Ovanesyan****, Colorado School of Mines, *D.M. Hausmann*, Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

The rapid shrinking of semiconductor devices has created a need for the low-temperature (≤400 °C) atomic layer deposition (ALD) of highly-conformal silicon nitride (SiN_x) and C-containing SiN_x films. However, to date, the ALD of these films remains challenging. In this work, we report the surface reaction mechanisms during the ALD of SiN_x and C-containing SiN_x for several ALD processes. Initially, our research focused on a baseline SiN_x ALD process that used alternating exposures of Si_2Cl_6 and NH_3 plasma. This process was subsequently modified by replacing the NH_3 plasma half-cycle with a CH_3NH_2 plasma to simultaneously incorporate both C and N. Finally, to overcome the limitations of SiN_x films deposited using H-containing plasmas, a three-step ALD process was developed that used Si_2Cl_6, CH_3NH_2, and N_2 plasma. The film composition, reactive surface sites, and adsorbed surface species were monitored using in situ attenuated total reflection Fourier transform infrared spectroscopy, which allowed us to elucidate the surface reaction mechanisms. In addition, in situ four-wavelength ellipsometry was used to obtain the growth per cycle (GPC). Ex situ analysis was used to obtain the conformality and elemental composition.

For the baseline Si_2Cl_6 and NH_3 plasma ALD process, our infrared spectra show that on a post-NH_3-plasma-treated SiN_x growth surface, Si_2Cl_6 reacts with surface $–NH_2$ species to form –NH and $–Si_xCl_{2x-1}$ (x = 1, 2) surface species. In the subsequent NH_3 plasma step, the $–Si_xCl_{2x-1}$ surface species are removed and the $–NH_2$ surface species are restored, allowing for the continuation of the ALD process. Film growth during the Si_2Cl_6 and CH_3NH_2 plasma ALD process occurs via an almost identical reaction mechanism, with the exception that C is incorporated in the form of -N=C=N- species during the CH_3NH_2 plasma step. In the three-step ALD process, Si_2Cl_6 again reacts with surface $–NH_2$ species, while in the CH_3NH_2 step, the CH_3NH_2 reacts with $–Si_xCl_{2x-1}$ surface species via the formation of Si-N linkages to form Si_2N-CH_3 surface species. During the N_2 plasma step, the Si_2N-CH_3 surface

*** TFD James Harper Award Finalist**

species are removed and the $–NH_2$ species are restored. When we compare the GPC and conformality (see Fig. 1) of the three-step ALD process to an aminosilane and N_2 plasma ALD process, we observe that the three-step ALD process has a higher conformality (~90%) and a higher GPC (~0.9 Å). However, these values are less than those reported for NH_3- or CH_3NH_2-plasma-based ALD processes. This suggests that the three-step ALD process behaves as an intermediate between an NH_3- or CH_3NH_2-plasma-based ALD process and an aminosilane and N_2 plasma ALD process.

5:20pm **PS+TF-ThA10 First-Principles Understanding and Kinetic Monte Carlo Analysis of Reaction Mechanisms in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride**, *G. Hartmann*, University of Texas at Austin, ***Peter Ventzek***, *J.P. Zhao*, Tokyo Electron America, *T. Iwao, K. Ishibashi*, Tokyo Electron Tohoku Limited, *G. Hwang*, University of Texas at Austin

Plasma enhanced ALD (PEALD) allows fabrication of high quality and ultra-conformal SiN deposition at low temperature. The PEALD of SiN films involves a repetitive two-step process of i) silicon-containing precursor adsorption/decomposition and ii) nitridation. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors and nitrogen, hydrogen or ammonia have been used as nitrogen precursors. Despite previous studies, the underlying reaction mechanisms of these Si precursors with a nitrogen containing surface during PEALD still remain uncertain. First-principles density-functional theory (DFT) calculations have been used to identify a novel mechanism for the adsorption and decomposition of DCS on a hydrogenated SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a relatively low barrier (< 0.3 eV), far lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the DCS adsorption and dissociation, notably the hypervalent nature of Si which permits chlorosilanes to adsorb prior to dissociation. A proper model of the interactions between the SiN surface are necessary to explain the ALD process and also indicate the mechanism for the formation of side products, which has a considerable contribution to the thermodynamic favorability of the proposed mechanism. Insights from the first principles calculations are incorporated into a Kinetic Monet Carlo Model (KMC) to illustrate different process scenarios. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to support Si precursor adsorption and dissociation.

5:40pm **PS+TF-ThA11** ***High Quality Crystalline AlN Films Produced by PEALD with Microwave ECR Plasma below 200 ºC***, ***Jesse Kalliomäki***, *V. Kilpi, T. Malinen*, Picosun Oy, Finland, *H. Enami, N. Mise*, Hitachi High-Technologies Corp., Japan, *H. Hamamura, T. Usui*, Hitachi R&D Group, Japan

Due to continuous feature size scaling down and change to the 3D structures new process innovations are now required more than ever. Conformal film formation of Al compounds such as AlN is one of the key technologies. AlN is widely used in thermal management applications and due to its compatibility with III–V compounds it has shown growing interest e.g. as interface material. There is also huge potential for AlN in MEMS manufacturing. PEALD at low temperature is one of the suitable solutions for these applications.

We have earlier reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1]. In present study, AlN film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. TMA (Trimethylaluminum) was used as Al precursor while nitrogen plasma was generated with M-ECR plasma generator to form AlN. Film properties such as density, crystallinity and conformality were studied. Composition of film was analyzed by XPS with Ar sputter.

AlN film properties were investigated as a function of deposition temperature as shown in **Fig. 1.** The film density increases with deposition temperature and at 200°C the density is 3.09g/cm^3, which is consistent for literature values for bulk AlN [2]. It was shown that longer N_2 plasma exposure time improved film density. The temperature series in **Fig. 1** shows that the growth rate was 0.57Å/c and 0.54Å/c at 100 and 250ºC, respectively. Interestingly, it was found a thickness dependent crystallization. For 20nm films deposited between 100 and 250ºC showed an amorphous structure, whereas 30nm film thickness and above show crystalline structure (verified by XRD) and higher roughness, see **Fig. 2**. Good quality films with conformality of < 0.5% (1σ non-uniformity) for 300mm wafer and high purity (C<1%, O<3%) were achieved. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [3] is supposed to improve the film properties.

The step coverage obtained in this study at AR 1:20 is >90% as shown in **Fig. 3.** This is promising for 3D device fabrication where conformal coating of high aspect ratios is crucial. From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next generation devices and opens the possibilities for beyond-silicon CMOS devices.

[1] H.Hamamura *et al.*, 16th International Conference on Atomic Layer Deposition (ALD2016)

[2] JCPDF 00-003-1144 (AlN)

[3] H.Enami *et al.*, submitted to ALD2017

Plasma Science and Technology Division
Room: 22 - Session PS+VT-ThA

Plasma Diagnostics, Sensors and Control
Moderator: Aranka Derzsi, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary

2:20pm **PS+VT-ThA1 Quantitative Analysis of Composition and Temperature of Semiconductor Processing Plasmas via Terahertz Spectroscopy**, ***Yaser Helal***, *C.F. Neese, F.C. De Lucia*, The Ohio State University, *A. Niabati, M. Johnson, B. Craver, P.J. Stout, M.D. Armacost*, Applied Materials, Inc.

Processing plasmas are at a similar pressure and temperature to the environment used to study atmospheric and astrophysical species in the terahertz (THz) spectral region. Many of the molecular neutrals, radicals, and ions present in processing plasmas have been studied in the laboratory and their absorption spectra have been cataloged or are in the literature for the purpose of astrophysical study. Recent developments in THz devices have made technology commercially available for applications outside of specialized laboratories. The methods developed over several decades in the THz spectral region for these laboratory studies are directly applicable to diagnostic measurements in the semiconductor manufacturing industry. In this work, a continuous wave, intensity calibrated THz absorption spectrometer was developed as a remote sensor of gas and plasma species. A major advantage of intensity calibrated rotational absorption spectroscopy is its ability to determine absolute concentrations and temperatures of molecular species from first principles without altering the plasma environment. An important part of this work was the design of the optical components which couple 500 – 750 GHz radiation through a commercial inductively coupled plasma (ICP) chamber. The measurement of transmission spectra was simultaneously fit for background and absorption signal. The measured absorption signal was used to calculate absolute densities and temperatures of polar species. Examples of measurements made in ICPs will be presented. Also, time resolved measurements were made and the time evolution of molecular densities will be discussed.

2:40pm **PS+VT-ThA2** ***In Situ*** **Measurement of Electron Emission Yields from Plasma-Exposed Surfaces**, ***Mark Sobolewski***, National Institute of Standards and Technology

Surfaces exposed to plasmas are bombarded by energetic particles which may induce electron emission. The emitted electrons may in turn influence the plasma. Accurate plasma simulations require knowledge of the flux or yields of emitted electrons. Yields can be measured directly in beam studies, but it is impractical to produce a beam of each possible energetic particle that could be produced by typical plasmas. In contrast, in-situ measurements, performed during plasma exposure, may provide useful values or bounds for effective or total electron emission yields, summed over all (or some subset) of the energetic particles present for given plasma conditions. Here, measurements were performed at 10 mTorr (1.3 Pa) in an inductively coupled plasma system equipped with an electrostatic shield and variable-frequency rf substrate bias. An insulating cap is placed on the rf-biased electrode to minimize edge effects. The cap also reduces the effective electrode size, which further limits any undesired effects of rf bias on the plasma and allows yield measurements on small substrates. The rf voltage and current across the sheath adjacent to the rf-biased electrode are measured and analyzed by detailed, numerical sheath models, which allow the current of electrons emitted from the surface to be distinguished from other mechanisms of current flow. The observed dependence on voltage and rf phase allows some discrimination between emission induced by energetic positive ions and that induced by photons and metastables. The technique is validated by comparing measurements made in argon discharges with literature results from beam studies and then is applied to plasma etching discharges in fluorocarbon gas mixtures.

3:00pm **PS+VT-ThA3 Studying Dynamic and Structured Plasma Systems Utilizing Laser-Collision Induced Fluorescence**, ***Edward Barnat***, *A. Fierro*, Sandia National Laboratories **INVITED**

Laser collision-induced fluorescence (LCIF) is a powerful diagnostic which can be used for making temporally and spatially resolved measurements of electron densities in a plasma discharge. The technique, which involves the measurement of optical emission emanating from higher energy excited states due to the redistribution of the lower energy laser-excited state by collisions with energetic plasma species, has been readily employed to study both helium and argon discharges. In this presentation, an overview of the fundamental principles and anticipated limitations of the LCIF method will be presented. Examples of the LCIF method applied to structured and dynamic discharges generated in helium and argon will be presented to demonstrate the utility of this diagnostic technique. Finally, recent efforts used to extend the LCIF method to higher pressure (near atmospheric pressure) discharges will be discussed.

4:00pm **PS+VT-ThA6 Effect of Ion Inertia on Ion Energy Broadness on Biased Electrode in Dual Frequency Capacitively Coupled Argon Plasma**, ***Yunchang Jang***, *H.-J. Roh, N.-K. Kim, S. Ryu, G.-H. Kim*, Seoul National University, Republic of Korea

Ion response time to RF sheath voltage is important to control the energy spread of ion energy distribution (IED) in the dual frequency capacitively coupled argon plasma. IED is known as being governed by the dynamics of ion in RF sheath and the magnitude of RF voltage peak. In previous study, semi-analytic models to determine IED were derived from concept of ion response time (τ_i). Ion energy broadness (ΔE_i) was represented in terms of the sheath voltage oscillation (V_{pp}) and τ_i/τ_{rf}. Ion response time was assumed as ion transit time across the sheath, τ_{ion} by adopting correction factor without thorough understanding. In this study, we investigate the underlying physics of the correction factor, consequently defining the ion response time τ_i with RF sheath voltage oscillation. Experiment were performed in dual frequency CCP at 20 mTorr of argon gas which has the ratio of maximum sheath size to ion mean free path ~ 2. Various ranges of RF bias (from τ_{ion}/τ_{rf} ~ 0.05 to τ_{ion}/τ_{rf} ~10) were applied to bottom electrode to enhance the incident ion energy with very high frequency (VHF, τ_i/τ_{rf} ~10) applied on the top electrode (showerhead) to sustain plasma. A commercial retarding field analyzer (Impedans, Vertex V4.0.10) was employed to measure IED. Plasma density, electron temperature and plasma potential were measured by using RF compensated Langmuir probe. Experimental results of ΔE_i to V_{pp} were compared with models under assumptions that ion response time is ion transit time across the sheath (τ_{ion}) or one of ion plasma frequency ($1/\omega_{pi}$). Experiment results revealed that the time scale of ion response time is determined by $1/\omega_{pi}$ rather than τ_{ion} in this high-density plasma. This result implies that ion response time is governed by the ion inertia at the sheath boundary to RF sheath oscillation. Ion inertia becomes the initial condition of ion acceleration and govern the ion energy arriving at surfaces.

4:20pm **PS+VT-ThA7 Collision Frequency Estimation using Microwave Hairpin Resonator Probes**, *D. Peterson*, ***Steven Shannon***, North Carolina State University

Microwave hairpin resonator probes have become convenient alternatives to Langmuir probes to measure electron density in low temperature plasmas. The impact of electron collisions with neutrals with regard to the analysis of the resonant frequency shift from which this density is determined has been well established.[1] In this work, a method for extracting the electron neutral collision frequency by measuring resonance broadening due to collisions is presented. By using both the resonance frequency and collision-broadened resonance width, the electron density and electron neutral collision frequency can be measured. Measurements are made in argon, oxygen, Ar/O_2, and helium plasmas sustained in an RF driven capacitive coupled parallel plate system operating in the 100's of mTorr to Torr range. Comparisons to calculated and modeled collision frequencies in single component background gases (Ar and He) are made; experimental results agree well with these conditions. Collision frequency measurements in more challenging regimes including molecular gases and gas mixes are also presented to demonstrate applicability across a broad range of pressures and gasses. Probe design, analysis methodology, and parametric trends in capacitive systems with regard to gas density, electron density, power density, and gas composition will be presented. This work is supported through a generous gift by Applied Materials Inc.

[1] *Plasma Sources Science and Technology* 16, no. 4 (2007): 716

4:40pm **PS+VT-ThA8 In-Situ Diagnostics of Processing Plasma and Semiconductor Films for High-Efficiency Silicon Hetero-Junction Solar Cells**, ***Shota Nunomura***, National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The plasma processing is a key technology for fabricating semiconductor devices such as solar cells, light-emitting diodes and transistors. In those devices, the semiconductor films are often prepared and/or post-processed by various plasma processes. During the processes, the films are exposed into the UV, radicals, and ions, and thereby the electronic property of the films is often degraded. So, the investigation of the plasma-material interaction is important for understanding the degradation mechanism and also for further developing the plasma processing technology.

Here, we show in-situ characterization of the electronic property of semiconductor films as well as the gas-phase plasma diagnostics during the plasma process. The process we diagnosed was PECVD of hydrogenated amorphous silicon (a-Si:H) for the passivation of silicon heterojunction solar cells. The plasma parameters and gas-phase spices, such as ions, radicals, and precursors are measured by using conventional techniques of Langmuir probe, quadrupole mass spectroscopy and optical emission spectroscopy [1-3]. Together with this gas-phase diagnostics, we measured the transport properties of the growing a-Si:H films such as carrier transport and trapping, by using a recently developed optical pump probe technique [4,5]. The optical property such as the bandgap, refractive index and extinction coefficient, was also characterized by real-time spectroscopic ellipsometry.

We found that transport property of the a-Si:H films was strongly limited by the defects generated during the PECVD process, and improved by post-deposition annealing process. The generated defects were distributed near the film surface; the defect rich surface layer was estimated to be less than approximately 10 nm. As for defect annihilation, the post deposition annealing was very efficient. The annealing temperate and period strongly influence the defect relaxation, inducing the improved carrier transport. The relation between the plasma process and transport property will be described in the presentation.

[1] S. Nunomura, I. Yoshida, and M. Kondo, *Appl. Phys. Lett*. **94**, 071502 (2009). [2] S. Nunomura and M. Kondo, *J. Appl. Phys.* **102**, 093306 (2007). [3] S. Nunomura. H. Katayama I. Yoshida, *Plasma Sources Sci. Technol.* **26**, 055018 (2017). [4] S. Nunomura, I. Sakata, and M. Kondo, *Appl. Phys. Express* **6**, 126201 (2013). [5] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014).

5:20pm **PS+VT-ThA10 Towards *In Situ* Microwave Imaging in Plasmas**, *A. Tselev*, University of Aveiro, Portugal, *J. Fagan*, NIST, ***Andrei Kolmakov***, CNST/NIST

There exists a great need for *in situ* nanoscale characterization of surface/interface morphologies during plasma treatments. These include plasma induced growth, surface modification, sputtering and other processes relevant to semiconductor and aerospace industries, environmental remediation and biomedical applications. To address these needs, the current approaches rely on either "post mortem" sample microscopy or *in situ* optical analytical methods. The latter, however, lack required nanoscale spatial resolution.

In this communication, we propose to use near-field microwave imaging known as scanning Microwave Impedance Microscopy (sMIM) to image processes in plasma. Different to optical microscopy, the sMIM is sensitive to variations of local permittivity and conductivity of the material under a scanning probe. We demonstrate applicability of the sMIM to monitor plasma-assisted processes with a submicron spatial resolution. In our approach, a plasma environment with an object of interest is separated from the sMIM probe and the rest of the microscope by a SiN membrane of a few-10s nm thickness, and the imaging is performed through this membrane. As a proof of concept, we were able to image carbon nanotube films drop-casted onto the SiN membranes and their transformations in the process of plasma-induced oxidation by a low-pressure air plasma. To the best of our knowledge this is the first report on application of an SPM for in situ imaging of plasma processing. The experiential limitations such as electromechanical and thermal stability of the membranes will be discussed.

5:40pm **PS+VT-ThA11 Probe System for Radical Species Characterization in Vacuum with Centimeter Spatial Resolution**, ***Ivan Shchelkanov***, *D. Qerimi, A. Hayes, J.T. Wegner, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Among plasma diagnostics one of the most difficult tasks is getting an estimate of radical gas species concentration in the ground state without plasma presence in the diagnosed volume. This is probably the major task for characterisation of downstream plasma composition in various areas of applied plasma technology and the requirements for characterisation tool are very strict. The ultimate device should have a good spatial resolution, relatively high response time, operate in highly reactive plasmas and in presence of sputtering flux materials, should be capable to characterize species of unknown geometrical distribution and composition.

The idea of a tool, which could satisfy most of the mentioned requirements, was proposed more than ten years ago [1] but only recently the Center for Plasma Materials Interaction was able to develop a complex system which can measure composition and density of radical species with 1 cm spatial-resolution and response time of 15 seconds in the presence of high intensity

RF fields and flux of sputtered material. The system can measure density of oxygen, nitrogen, and hydrogen radicals, when different species present in the chamber at the same time. For vacuum chamber of 13 inch in diameter and 46 inches tall, which is equipped with 1 kW Helicon plasma source , the measured density at ~75 mTorr, 1kW power and 10 inch from the source, the density of radical species of hydrogen was 0.7 [±0.5] $*10^{21}$ m^{-3} and of nitrogen radicals it was 1.1 [±0.7] $*10^{20}$ m^{-3}. Additional comparison with zero dimensional model showed a match with-in an errorbar between an experiment and the model.[2]

The principle of the radical species concentration measurement is the following. The thermocouple tip is coated with a particular catalytic metal. Once the probe is exposed to the gas atoms, recombination of gas atoms occurs on the surface of the probe tip. The catalytic surface provides efficient recombination thus more energy is delivered to the surface from the recombination reaction [3] compared to a probe tip without the catalytic surface. By measuring the temperature of the probe it becomes possible to quantify the amount of gas atoms in the probe vicinity. Different radical species can be distinguished by using catalytic surfaces particular to the species in question. Current work is focused on radical probe system capabilities, physical limitations, and examples of characterized plasmas.

References:

1. M. Mozetic / Vacuum V.47 #6-8 pages 943 to 945 (1996)

2. D.T. Elg / *J. Micro/Nanolith. MEMS MOEMS, 16, 023501 (2017)*

3. M. Mozetic / Surface & Coatings Technology 201 (2007) 4837–484

6:00pm **PS+VT-ThA12 Spatiotemporal Evolution of RF Magnetic Field and Plasma Current in a Very High Frequency Plasma Source**, ***Jianping Zhao***, *P.L.G. Ventzek, B. Lane, C. Campbell*, Tokyo Electron America, *T. Iwao, K. Ishibashi*, Tokyo Electron Limited

Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion bombardment energy, ostensibly to minimize damage, high ion and radical flux to the substrate. The benefits of VHF are accompanied by challenges. The short wavelength associated with VHF source power is reduced even further in the presence of high density plasma. The wavelengths are comparable to the RF electrode dimension. High plasma densities can also lead to skin effects that screen the electromagnetic fields from parts of the plasma. As a result, spatial variations in plasma density and sheath voltage can arise and lead to undesired non-uniformities in process parameters such as etch or deposition rate. E to H transitions and plasma-sheath local resonances are other potential destroyers of plasma uniformity. Resonances and mode jumping can potentially prevent smooth plasma property control through adjustable process parameter changes. In order to understand these fundamental electromagnetic effects on VHF plasma non-uniformity to achieve a better design of plasma source, it is desired to have a detailed investigation on the spatial and temporal evolution of RF magnetic field and plasma current spanning a large RF power, pressure, and chemistry range. We present here a time and phase resolved measurements of the spatial structure of the electromagnetic waves in a 100MHz plasma source performed with a magnetic field probe (B-dot loop). The probe was translated across the diameter of the VHF plasma, measuring the magnitude and phase of the fundamental and harmonics of the plasma excitation frequency as a function of radial position. The measured magnetic fields displayed a transition from simple to complex behaviors depending on plasma conditions. The spatiotemporal resolved magnetic field exhibits a series of fast current reversal and subsequent circulation driven by inward wave propagation that are electromagnetic in nature. We show how the onset, frequency and amplitude of the current reversal and subsequent circulation are strongly related to applied plasma conditions (e.g., density, sheath thickness). We also show that plasma current derived from the magnetic field distribution is closely correlated to the plasma density profile measured by a plasma absorption probe.

Plasma Science and Technology Division
Room: 23 - Session PS+NS+SS+TF-FrM

Atomic Layer Etching II

Moderator: Edward Barnat, Sandia National Laboratories

8:20am **PS+NS+SS+TF-FrM1 Quasi-Atomic Layer Etching of Silicon Nitride with Independent Control of Directionality and Selectivity**, ***Sonam Sherpa***, *P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited

Atomic layer etching (ALE) has emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma. The underlying premise was the surface modification via implantation of hydrogen ions into silicon nitride resulting in an anisotropic etch.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride with the resultant etch being isotropic. These results confirm the realization of self-limiting etch of silicon nitride with tunable directionality. This tuning capability is critical for sub-7nm technology node. Illustrations of anisotropic (spacer RIE for self-aligned multiple patterning) and isotropic (spacer RIE for nanowire FET) etch by using this process will also be discussed. Selectivity to oxide is > 100 and damage to underlying silicon can be minimized by optimizing the flux of atomic fluorine during the exposure to fluorinated plasma. Thus, hydrogen plasma controls the directionality while fluorinated plasma step determines the selectivity to oxide and underlying silicon.

8:40am **PS+NS+SS+TF-FrM2 WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms**, ***Nicholas Johnson***, *S.M. George*, University of Colorado at Boulder

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both WO_3 ALE and W ALE as W oxidation to WO_3 is needed to define self-limiting reactions for W ALE.

WO_3 ALE was demonstrated using an AB exposure sequence with boron trichloride (BCl_3) and hydrogen fluoride (HF). BCl_3 and HF etch WO_3 by a "conversion-fluorination" mechanism. The BCl_3 converts the WO_3 surface to a B_2O_3 layer while forming volatile WO_xCl_y. HF then spontaneously etches the B_2O_3 layer producing volatile BF_3 and H_2O products. WO_3 films were formed by oxidizing W ALD films with an oxygen plasma at 280ºC. *In situ* spectroscopic ellipsometry (SE) studies determined that the BCl_3 and HF reactions were self-limiting versus exposure. WO_3 ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because BCl_3 and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a WO_3 layer and then the WO_3 layer is etched with BCl_3 and HF. SE could simultaneously monitor the W and WO_3 thicknesses and conversion of W to WO_3. Oxidation of the W surface was performed using O_3. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. W ALE was shown to be self-limiting with respect to each part of the ABC process. The etch rates for W ALE were 2.4 Å/cycle at 207°C. An oxide thickness of ~20Å remained during W ALE, but could be removed with BCl_3/HF without affecting the W layer.

[1] Younghee Lee, et al., "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994-3003 (2016).

[2] Nicholas R. Johnson, et al., "Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

9:00am **PS+NS+SS+TF-FrM3 Solving the Grand Challenges of Plasma Etch with Concurrent Engineering**, ***Mingmei Wang***, TEL Technology Center, America, LLC, *P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited **INVITED**

A consequence of multiple patterning approaches enabling Moore's Law scaling to continue through 10nm to 7nm and beyond is that plasma dry etch process faces unprecedented challenges. "Scaling" of plasma etch to seemingly impossible capabilities is the key to meeting Moore's Law scaling. For example, etch process must achieve extremely high (almost infinite) selectivity in applications where self aligned patterning schemes are involved. Etch process is also required to achieve less than half nanometer (atomic scale) CD variations across 300mm wafers including the important "extreme edge" area as small as 2mm exclusion. These are but two examples of etch grand challenges. While the process requirements push the hardware design to the limits, understanding of process mechanisms becomes the most critical bottleneck to explore process regimes that are able to satisfy the most challenging patterning requirements. In fact, without process understanding at the atomic scale, it is difficult to imagine a means to innovate hardware designs.

In this talk, we will discuss concurrent engineering approaches including both modeling and experiment to understand and develop etching processes that meet grand challenge requirements. The core of the approach is an integrated chamber scale HPEM (Hybrid Plasma Equipment Model)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [1]. The concurrent engineering approach comprises stages of development and prediction capability tests using both blanket wafer and patterned stack data and finally process parameter optimization. By using this approach, we are able to provide insights on how to resolve grand challenges in plasma etch with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a few case studies in SAC quasi-ALE [2], Si ALE, organic etch CD uniformity, and LER/LWR improvement in EUV resist patterned sample etch. Furthermore, insights into the relationship between chamber function and critical surface interactions will be discussed.

[1] M.Wang and M.Kushner, J. Appl. Phys 107, 2010.

[2] M.Wang, P. Ventzek, A. Ranjan, J. Vac. Sci. Technol. A 35, 2017.

9:40am **PS+NS+SS+TF-FrM5 Effect of Non-Uniform Polymer Deposition on the Atomic Layer Etching of 3D Features in SiO_2**, ***Chad Huard***, University of Michigan, *Y. Zhang, S. Sriraman, A. Paterson*, Lam Research Corporation, *M.J. Kushner*, University of Michigan

Atomic layer etching (ALE) typically separates the etch process into (at least) two self-limited steps, repeated cyclically – a passivation and an etch step. To obtain all of the benefits of ALE, each of the steps should be fully self-limited, and produce no continuous etching during either step. Only by the synergy between the two steps being repeated cyclically is atomic etching achieved. ALE etching mechanisms have been demonstrated for several materials (e.g., Si, Ge) that do not involve thick passivation layers. ALE-like etching has also been demonstrated for SiO_2 and Si_3N_4, however with the etching mechanisms for these materials relying on the non-self-limited deposition of a polymer layer, it is more difficult to obtain the full benefits of ALE in these systems.

To investigate the benefits and limitations of using an ALE-like pulsing scheme for etching SiO_2, a representation of the through-polymer etching mechanism of SiO_2 in $Ar/C_4F_8/O_2$ plasmas was developed and implemented into the 3-dimensional Monte Carlo Feature Profile Model (MCFPM). The model includes diffusion of radical atomic species (F and O) through the polymer capping layer and ion-energy activated reactions at the SiO_2/polymer interface stimulated by ions implanting through the polymer capping layer. These processes allow for the simulation of SiO_2 (and Si) etching through a finite thickness of polymer. The model reproduces systematic trends for selectivity and etch rates as a function of polymer thickness observed for continuous etching.

Results from the model suggest that the non-self-limited nature of the polymer deposition step can limit the benefits of applying ALE techniques to SiO_2, particularly in 3D features. The balance of polymer deposition by radical CF_x species and erosion by F radicals is subject to neutral transport issues and so are more sensitive to geometry and aspect ratio than for fully self-limited passivation, as occurs in ALE of Si using, for example, Cl_2 containing gases. The reactive sticking coefficients of CF_x radicals on the polymer surface depends, in part, on ion generated dangling bonds which can result in a non-uniform polymer thickness in 3D features. The etch depth per cycle (EPC) was found to depend on polymer thickness, introducing non-uniformity and aspect ratio dependent etch rates in 3D features during ALE.

Methods for mitigating the dependence of EPC on polymer thickness using carefully controlled ion energies and the introduction of O_2 will be discussed.

Work was supported by Lam Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

10:00am **PS+NS+SS+TF-FrM6 Etching with Low Te Plasmas**, ***Scott Walton***, *D.R. Boris, S.C. Hernández,* Naval Research Laboratory, *S.G. Rosenberg*, ASEE Postdoctoral Fellow, NRL, *H. Miyazoe, A.V. Jagtiani, S.U. Engelmann, E.A. Joseph*, IBM T.J. Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{11} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. The flux at the surface will thus be characterized by a comparatively large amount of ions whose energies are < 5 eV, a value commensurate with the bond strength of most materials. Ion energies can be raised with substrate biasing, which makes these sources well-suited to meet the needs of energy requirements for precise, selective etching. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

10:20am **PS+NS+SS+TF-FrM7 Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Oxidation and Fluorination Reactions**, ***Younghee Lee***, *S.M. George*, University of Colorado at Boulder

Titanium nitride (TiN) is an important conducting material as a copper diffusion barrier and a gate electrode in semiconductor devices. Previous thermal atomic layer etching (ALE) studies have shown that TiN was not etched using fluorination and ligand-exchange reactions [1]. These results suggest that the ligand-exchange reactions do not produce stable and volatile reaction products.

In this work, a new etching mechanism based on sequential, self-limiting oxidation and fluorination reactions was developed for thermal TiN ALE. The oxidation reactant was either O_3 or H_2O_2. The fluorination reactant was hydrogen fluoride (HF) derived from HF-pyridine. In the proposed reaction mechanism, the O_3 reaction oxidizes the surface of the TiN substrate to a TiO_2 layer and produces gaseous products such as NO. HF exposure to the TiO_2 layer then yields TiF_4 and H_2O as volatile reaction products. The overall reaction can be written as: $TiN + 3O_3 + 4HF \rightarrow TiF_4 + 3O_2 + NO + 2H_2O$.

Quartz crystal microbalance experiments showed that HF can spontaneously etch TiO_2 films. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that TiN films were etched linearly versus the number of ALE cycles using O_3 and HF as the reactants. The etch rate for TiN ALE was determined at temperatures from 150 to 350°C. The etch rates increased with temperature from 0.06 Å/cycle at 150°C to 0.20 Å/cycle at 250°C and stayed nearly constant for temperatures ≥250°C

The thermal ALE of many other metal nitrides should be possible using this new etching mechanism based on oxidation and fluorination reactions. This thermal ALE mechanism should also be applicable to metal carbides, metal sulfides, metal selenides, and elemental metals that have volatile metal fluorides.

[1] Y. Lee, C. Huffman and S.M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.* **28**, 7657 (2016).

10:40am **PS+NS+SS+TF-FrM8 Atomistic Simulations of H_2 Plasma Modification of SiN Thin-Films for Advanced Etch Processes**, ***Vahagn Martirosyan***, *E. Despiau-Pujo, O. Joubert*, LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the active layers of advanced nanoelectronic devices. In particular, silicon nitride or low-k spacers etching must be performed with nanoscale-precision without creating defects to the underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To solve this problem, one possible alternative is to use a recently developed etch technology, which consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the successful development of such a new etch approach requires a more detailed understanding of the fundamental mechanisms involved in the process. Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-N-He and Si-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand the role of ion energy in the self-limited ion implantation, and to determine the relationship between the flux/energy of plasma species bombarding the surface and its chemical/structural modifications.

In this work, we investigate the interaction between hydrogen plasma species (Hx+ ions and H radicals) and silicon nitride via MD simulations. We first study the impact of ion energy (5-100eV), ion dose and ion type on a SiN substrate only exposed to ion bombardment. Then, the influence of a mixed exposure to both Hx+ ions and atomic H is investigated to observe how the hydrogen plasma composition will affect the SiN substrate modification. For pure ion bombardment conditions, simulations show an initial Hx+ ion implantation followed by the formation of a stable modified layer at steady state. Few or no SiN etching is observed for ion energies >25eV, which shows that hydrogen ions only induce a volume transformation and can modify the SiN substrate on a precise depth without etching it. By contrast, simulations of mixed ion/radical bombardment show that a high concentration of atomic hydrogen can crucially change the evolution of the substrate, since H radicals are able to slowly etch SiN along with the modification caused by Hx+ ions. Mechanisms of aforementioned phenomena, as well as comparison with experiments, will be discussed during the presentation.

1. N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

11:00am **PS+NS+SS+TF-FrM9 Defectless Nanostructure Patterning of Germanium Using Neutral Beam Etching for Ge FinFET Devices**, ***Shuichi Noda***, Tohoku University, Japan, *W. Mizubayashi, K. Endo*, AIST, Japan, *S. Samukawa*, Tohoku Univeversity, AIST, Japan

Germanium FinFET has been becoming a promising candidates for highly scaled CMOS FETs due to large carrier mobility. However, etching mechanisms of Ge and optimization of etching method have not investigated deeply. We have already succeeded to apply a neutral beam etching (NBE) method to Si FinFET fabrication processes and shown excellent device performances owing to low-damage properties of NBE [1]. Since Ge is much more unstable material to apply to FET devices than Si, there must be much more advantages to use NBE method.

The NBE system consists of an inductive coupled plasma (ICP) source and a carbon aperture plate (neutralization plate) on which enormous number of high aspect ratio aperture holes are opened. Positive and negative chlorine ions generated in a pulse time modulated ICP are accelerated toward the aperture plate and effectively converted to the neutral beam by applying rf field on the aperture plate. Etching substrates beneath the aperture plate are etched mainly by directional chlorine neutral beams without any risky matters such as charged particles (electrons and ions) and irradiation of vacuum ultra-violet (VUV) light. We consider that the VUV irradiation has notable effect on the etching characteristics and defect generation that influences device performances.

We compared etching characteristics of Ge between the NBE and a plasma etching using the same ICP source. It was found that the Ge etching rate of NBE was about one order of magnitude smaller than that of the plasma etching. We consider that such a large differences is caused by surface defects induced by the VUV irradiation. Under the VUV irradiation, surface defects, that is high density dangling bonds of Ge, are created and the defect sites react with chlorine radicals actively and the chlorinated layer are etched off by the ion bombardment in the case of the plasma etching. On the other side, the Ge surface exposed to the neutral beam seems to be chlorinated more slowly and probably the chlorinated layer is much thinner than the plasma-like conditions. And the etching reaction occurs by the chlorine neutral atom beam bombardment. This smaller etch rate around 20 nm/min seems a little bit inefficient however it can be said this small etch rate is much more useful characteristics for the nanometer scale low damage etching processes. AFM observation showed that the etched surfaces by NBE were much smoother than that by the plasma etching. Etched side wall (to be Ge channel surface) by NBE were also very smooth and vertical. High magnification TEM images showed substantially atomic revel smooth side wall.

[1] K. Endo *et al.*, IEDM Tech. Dig. (2005) pp. 840-843.

11:20am **PS+NS+SS+TF-FrM10 Thermally-Driven Atomic Layer Etching of Metallic Tungsten Films Using O_2 and WF_6**, ***Wenyi Xie***, *P.C. Lemaire, G.N. Parsons*, North Carolina State University

The semiconductor industry is facing the challenge of manufacturing transistor devices with sub-10 nm high aspect ratio features. Understanding and developing self-limiting etching processes that allow precise control over the thickness of materials removed is essential for enabling the manufacturing complex transistor structures. In this work, we investigated chemical vapor etching of tungsten films using oxygen (O_2) as the oxidant source and tungsten hexafluoride (WF_6) as the etchant.

We propose that etching of tungsten proceeds in two steps: 1) oxidation of the tungsten film to form WO_x surface species and 2) formation and removal of volatile metal fluoride species upon reaction with WF_6. Using quartz crystal microbalance (QCM), we found that the oxidation step with O_2 is required for etching to occur during WF_6 exposure. In addition, etching of O_2 treated tungsten films showed saturation towards WF_6 exposure. This indicates that etching of tungsten using oxygen and WF_6 is a self-limiting process, making it promising as an atomic layer etching process. QCM results also showed that the rate of etching depends on the temperature. Minimal amount of etching was measured at temperatures less than 275 °C. Ex-situ characterization techniques were applied to analyze the etching of tungsten films deposited on SiO_2 substrates. Scanning electron microscopy (SEM) results revealed the change in morphology of tungsten films after different number of O_2-WF_6 ALE cycles. The tungsten film on SiO_2 started out as a coalesced film, which transformed into disjointed nuclei, and the nuclei appeared completely removed as the number ALE cycle increased. Lastly, X-ray photoelectron spectroscopy (XPS) analyses further confirmed etching of tungsten film and showed a minimal amount of fluorine remained on the surface after the O_2-WF_6 ALE process.

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