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 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).

* **Coburn & Winters Student Award Finalist**

[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.

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