

# Wednesday Afternoon, October 21, 2015

## Plasma Science and Technology

Room: 210B - Session PS+AS+SS-WeA

### Plasma Surface Interactions

Moderator: Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+AS+SS-WeA1 *In Situ* FTIR Diagnostics and Characterization of Etch By-Product Deposition on Chamber Walls and Wafer Surface during Halogen Etching of Silicon, Neema Rastgar, S. Sriraman, R. Marsh, A. Paterson,** Lam Research Corporation

Plasma etching is a critical technology for nanoelectronics fabrication, but the use of a vacuum chamber limits the number of in situ, real-time diagnostics measurements that can be performed during an etch process. Byproduct deposition on chamber walls during etching can affect the run-to-run performance of an etch process if there is build-up or change of wall characteristics with time. Knowledge of chamber wall evolution and the composition of wall-deposited films are critical to understanding the performance of plasma etch processes, and an in situ diagnostics measurement is useful for monitoring the chamber walls in real time.

In this talk, we report the use of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to perform in situ diagnostics of a vacuum chamber's walls during plasma etching. Using ATR-FTIR, the relative thickness and makeup of chamber wall deposits in real time is monitored. This information is then used to develop a chamber wall cleaning process in order to maintain reproducible etching conditions from wafer to wafer. In particular, we report mid-IR (4000-650  $\text{cm}^{-1}$ ) absorption spectra of chamber wall-deposited silicon byproducts formed during halogen etching of silicon wafers. Preliminary results demonstrating measurements of on-wafer etch byproduct evolution as well as its correlation to chamber wall deposits will be discussed.

2:40pm **PS+AS+SS-WeA2 Particle as a Temperature Probe: Thermal Effects in Non-Thermal Plasmas, Thomas Lopez, L. Mangolini,** University of California Riverside

Silicon nanocrystals are currently under investigation for several applications including nanoelectronics, light emitting devices, photovoltaics, thermal electric devices, and energy recovery and storage. Continuous flow nonthermal plasmas reactors are ideal for silicon nanoparticle production for many reasons; continuous flow non thermal plasma reactors are a scalable system, they readily produce completely amorphous to completely crystalline samples, and they have the ability to control size and size distributions of produced particles [1]. Extensive *in-situ* and *ex-situ* characterization on continuous flow non-thermal plasma reactors has been carried out characterizing nucleation, growth, and structural evolution [2]. Particle size, structure, and surface termination are all particle properties that are directly correlated to the particles' interactions with ions and other plasma produced radicals during their creation [2]. It has been shown that the interactions between particles, ions and other radicals in non-thermal plasmas leads to a thermal annealing process [3], meaning particles in non-thermal plasmas are heated well above the temperatures of their respective carrier gases. We probe the temperature of silicon nanoparticles produced via continuous flow non-thermal plasma reactors by monitoring their surface termination. *In-situ* FTIR has been utilized to track changes in the surface chemistry of particles, which have then been correlated to the particle temperature as a function of plasma power. FTIR data shows that hydrogen termination of silicon nanoparticles as they flow through a plasma is power dependent, with higher power leading to a decrease in hydrogen surface termination. We attribute this behaviour to thermally induced desorption from the particle surface. A discussion on the characterization of nanoparticle interactions with the plasma based on *in-situ* FTIR, optical emission spectroscopy and ion density measurements will be presented.

1. Lopez, T. and L. Mangolini, *Low activation energy for the crystallization of amorphous silicon nanoparticles*, *Nanoscale*, 2014. **6**(3): p. 1286-1294
2. Lopez, Thomas, and Lorenzo Mangolini. *Journal of Vacuum Science & Technology B* 32.6 (2014): 061802.
3. Kramer, N.J., R.J. Anthony, M. Mamunuru, E.S. Aydil, and U.R. Kortshagen, *Plasma-induced crystallization of silicon nanoparticles*, *Journal of Physics D: Applied Physics*, 2014. **47**(7): p. 075202.

3:00pm **PS+AS+SS-WeA3 Plasma-Surface Interactions at Low and High Pressure, Vincent Donnelly,** University of Houston **INVITED**

This talk will review studied of the interactions of low pressure  $\text{Cl}_2$ , HBr, and  $\text{O}_2$  inductively-coupled plasmas with reactor chamber walls, with and

without Si etching, using the "spinning wall" technique. The spinning wall is part of the reactor chamber walls, allowing near-real-time analysis of the composition of surface layers via Auger electron spectrometry, and determination of species desorbing off the walls by mass spectrometry. Langmuir-Hinshelwood (L-H) reactions, with surface residence times  $> 0.5$  ms can be studied by this technique. Many commonalities were found for the different source gas plasmas. For example, when the walls were coated with  $\text{SiO}_x$  or  $\text{AlO}_x$  layers, A + B recombination reactions including  $\text{O} + \text{O}$ ,  $\text{O} + \text{Cl}$ ,  $\text{Cl} + \text{Cl}$  and  $\text{H} + \text{Br}$  are detected, provided that the surface contains a level of oxygen above some critical value. During Si etching, surfaces coated with Si-halide products tend to be less catalytic toward L-H recombination reactions, while Si-oxyhalides films formed on chamber walls when oxygen is present in the plasma are much more active in promoting L-H recombination, as well as adsorption and delayed desorption of  $\text{Cl}_2$ . At most sites, O is believed to be in the inactive form of Si-O-Si. In relatively few cases, O cannot coordinate to a second Si and the active Si-O- forms. This quickly forms Si-O-A and then mobile B on the surface forms Si-O-AB, followed by desorption of AB, which could also be delayed. For all of the products observed, formation and desorption of AB is exothermic. Si etching with small oxygen addition leads to "sticky" products with a range of masses up to at least the limit of our mass spectrometer ( $m/e = 500$ ) that desorb from chamber wall surfaces in ms to min after plasma exposure. Gaseous products contain -O-Si-O- linkages are prominent, in addition to Si-mono and tri-halides. In HBr-containing plasmas, products contain little or no H. Experiments have also begun to study plasma-surface interactions at atmospheric pressure. Species present within one mean free path of a quartz substrate exposed to a He jet plasma in ambient air and in a sealed chamber with gas additives are spatially resolved using a new near-field optical emission spectroscopy method.

4:20pm **PS+AS+SS-WeA7 Measurements of IIEE Emitted Electrons from Chemically-Cleaned and Sputtered-Cleaned Semiconductor Surfaces, D. Urrabazo, Lawrence Overzet,** University of Texas at Dallas

Plasma-surface interactions with semiconductors comprise a variety of interesting phenomena in addition to etching and deposition. One such phenomenon is ion induced electron emission (IIEE). IIEE has historically been viewed as extremely surface sensitive; but recent measurements have suggested that the IIEE yield from semiconductors, unlike metals, may in fact depend on the sub-surface properties as well. We investigated the effects of the surface and sub-surface properties (doping type, Fermi level, cleanliness level) on the relative IIEE yields from Si and Ge. Our measurements indicate that the relative IIEE yields did not depend on the doping type to a significant degree independent of the level of cleanliness. This result is consistent with IIEE theory. We further explored the sensitivity of the IIEE yield to surface cleanliness by making XPS and UPS measurements on the surface chemistry and approximate surface density of states (sDOS) of the semiconductors. By combining the theoretical IIEE model with the sDOS, we were able to replicate the changes in the IIEE emitted electron distribution functions due to surface cleanliness changes. Thus, we confirmed that the IIEE yield is affected by the cleanliness of the surface primarily through the change in the surface density of states.

Acknowledgement: This material is based upon work supported by the Department of Energy under Award Number DE-SC-0009308.

4:40pm **PS+AS+SS-WeA8 Effects of Hydrogen on Etching Processes for Transparent Conducting Films, Hu Li\*, K. Karahashi,** Osaka University, Japan, *M. Fukasawa, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan, *S. Hamaguchi,* Osaka University, Japan

The market demand for high-resolution optoelectronic devices such as head-mounted displays has accelerated the development of micro pattern formation technologies for transparent conducting oxides (TCOs) with a pattern resolution of sub-microns or even nanometers. Reactive ion etching (RIE), which has been widely used in the fabrication of semiconductors, is also a promising technology for patterning of TCOs. Tin-doped indium oxide (ITO) and Zinc oxide (ZnO) are widely used TCOs in the industry. The goal of this study is therefore to establish RIE technologies for ITO and ZnO for high-resolution patterning.

Typical RIE processes for ITO and ZnO use plasmas based on organic gases such as  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ .  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  are non-corrosive gases and RIE processes with such gases are expected to achieve high etching rates with less process damages. In this study, we have mostly focused on ZnO etching processes and evaluated sputtering yields and analyzed surface reaction characteristics of ZnO by various chemically reactive species such as  $\text{CH}_x^+$ ,  $\text{H}^+$ , and  $\text{H}^*$ , using a mass-selected ion beam system. The mass-

\* Coburn & Winters Student Award Finalist

selected ion beam system allows one to examine surface reactions caused by specific ion species with a given incident energy incident upon the sample substrate set in an ultra-high vacuum (UHV) reaction chamber. Simultaneous injection of hydrogen radicals have been also performed with a hydrogen radical source. Surface chemical composition after such beam injections have been analyzed by *in-situ* X-ray Photoelectron Spectroscopy (XPS) installed in the reaction chamber.

Our previous study [1] found that the sputtering yield of ZnO strongly depends on the number of hydrogen atoms contained in each incident molecular ions. In this study, we have clarified the effects of incident hydrogen ions and radicals. When ZnO is etched by simultaneous injection of energetic  $\text{CH}^+$  ions and abundant hydrogen radicals, it has been found that etching proceeds with no carbon deposition and the sputtering yield of ZnO is closed to that of the corresponding physical sputtering. This result suggests that hydrogen radicals prevent carbon accumulation on ZnO and energetic hydrogen ion incidence leads to the formation of a surface damage layer, which is more easily sputtered by incident energetic ions. Therefore the presence of  $\text{CH}_3^+$  ions is not indispensable in such a RIE process and the embrittlement of ZnO by hydrogen is more crucial to the achievement of efficient etching processes for ZnO.

[1] H. Li, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, AVS61st Int. Symp. Exh. Abst. 4892, PS-TuM11.

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5:00pm **PS+AS+SS-WeA9 Mechanisms of Hydrocarbon Based Polymer Etch using Pulsed Plasmas**, Barton Lane, P. Ventzek, M. Matsukuma, A. Suzuki, A. Koshiishi, Tokyo Electron Limited

Dry etch of hydrocarbon based polymers is important for semiconductor device manufacturing. The etch mechanisms for oxygen rich plasma etch of hydrocarbon based polymers has been studied but the mechanism for lean chemistries has received little attention. We report on an experimental and analytic study of the mechanism for etching of a hydrocarbon based polymer using an Ar/O<sub>2</sub> chemistry in a single frequency 13.56 MHz test bed. The experimental study employs an analysis of transients from sequential oxidation and Ar sputtering steps using OES and surface analytics to constrain conceptual models for the etch mechanism. The conceptual model is consistent with observations from MD studies and surface analysis performed by Vegh, et al. and Ohrlein, et al. [1,2] and other similar studies. Parameters of the model are fit using published data and the experimentally observed time scales. [1] J.J. Vegh, D. Nest, D. B. Graves, R. Bruce, S. Englemann, T. Kwon, R. J. Phaneuf, G. S. Ohrlein, B. K. Long, and C. G. Willson, *Jour. of Applied Physics* **104**, 034308 (2008), [2] G.S. Ohrlein, R. J. Phaneuf, D. G. Graves, *J. Vac. Sci. Tech. B* **29**, 010801-1 (2011).

5:20pm **PS+AS+SS-WeA10 Role of Plasma Density in Damage Characterization and its Impact on Low-Damage Plasma Process Design**, Koji Eriguchi, M. Kamei, Y. Nakakubo, K. Ono, Kyoto University, Japan

Plasma process-induced damage (PID) is one of critical issues in designing metal-oxide-semiconductor field-effect transistors (MOSFETs) with higher performance and reliability. The damage creation mechanisms—plasma-induced physical damage (PPD) and charging damage (PCD) [1]—have been characterized by various techniques so far [2] to design low plasma processes. In this study, conflicting results leading to erroneous conclusions in designing future plasma processes are presented, where ion flux and charge injection from plasma (~ plasma density) play a key role in these conventional characterizations. Firstly, regarding PPD, n-type (100) Si wafers were exposed to Ar-based ICP and CCP discharges [3] and the localized defects were created in the Si substrates by ion bombardment. It is found that, although the average energy of incident ions ( $E_{\text{ion}}$ ) is larger for the case of CCP, the latent defect density ( $n_{\text{dam}}$ ) of CCP-damaged samples is smaller than that of ICP, even after the damaged-layer removal. This observation is in sharp contrast to previous pictures, i.e., the larger  $E_{\text{ion}}$  leads to the larger PPD. Secondly, MOSFETs with "high-k" ( $\text{HfSiO}_x$ ) gate dielectric were damaged by the Ar-based ICP plasma and the high-k damage (~ carrier trap site generation) by PCD is evaluated by time-dependent dielectric breakdown (TDDB) measurement [4]. We identify that the TDDB lifetime becomes longer under a certain amount of charge injection by plasma-induced current. This finding implies that one might be misled to an erroneous design rule of future LSIs. We propose a model explaining these conflicting results, where both ion flux and charge injection from plasma and the nature of the analysis techniques are taken into account. Since modern FinFETs with high-k dielectrics [5] are

susceptible to PPD and PCD, the present model should be intensively implemented in designing future "low-damage" plasma processes.

This work was supported in part by a Grant-in-Aid for Scientific Research (B) 25630293 from the Japan Society for the Promotion of Science.

[1] For example, K. Eriguchi and K. Ono, *J. Phys. D* **41**, 024002 (2008).

[2] M. Fukasawa et al., *Dry Process Symposium*, 183, (2013).

[3] Y. Nakakubo et al., *ECS J. Solid State Sci. Technol.*, **4** N5077 (2015).

[4] M. Kamei et al., *IEEE Int. Integrated Reliability Workshop Final Report*, 43 (2014).

[5] For example, I. Ferain et al., *Nature* **479**, 310 (2011).

5:40pm **PS+AS+SS-WeA11 Dry Deep Etching Of Bulk Titanium By Plasma Processes**, Edouard Laudrel, T. Tillocher, P. Lefauchaux, GREMI CNRS/Université d'Orléans, France, B. Boutaud, Sorin Crm, France, R. Dussart, GREMI CNRS/Université d'Orléans, France

Bio-MEMS have emerged these last years with applications for biosensors, drug delivery, etc. The biocompatibility, the mechanical strength and the hydrophilicity properties have made titanium a widely used material with a great interest in the biomedical field. This element was chosen to fabricate body implantable devices with the help of microfabrication methods from microelectronics technologies in order to pattern structures with vertical sidewalls and smooth surfaces. Most of the literature with an interest in titanium deep etching relies on chlorine plasma processes. They are performed at room temperature of the substrate with typical etch rates close to  $1 \mu\text{m}\cdot\text{min}^{-1}$  and provide rather smooth surfaces.  $\text{TiO}_2$  or Ni are typically used as hard mask. However, a thick (several 10s of microns) SU8 layer, which is a negative photoresist, has also been reported as an alternative mask because it can be easily patterned and stripped.

Samples used in our experiments consist of coupons of a patterned titanium wafer glued on a silicon carrier wafer. The titanium wafer is  $300 \mu\text{m}$  thick with a  $15 \mu\text{m}$  thick backside thermal  $\text{TiO}_2$  layer and the mask is a  $15 \mu\text{m}$  electrochemically deposited thick nickel layer. The samples were processed in two different ICP reactors. Two different chemistries can be used to etch titanium. A chlorine-based chemistry at low pressure can be used to obtain anisotropic profiles but with reduced etch rates at room temperature. With the first reactor, equipped with a diffusion chamber, titanium etch rate was  $1 \mu\text{m}\cdot\text{min}^{-1}$ . A fluorine-based chemistry admits higher etch rate (as  $4 \mu\text{m}\cdot\text{min}^{-1}$ ) at higher pressure (few Pa) with isotropic profiles if the sample temperature is sufficient to form volatile etch by-products. Both chemistries, as well as  $\text{Cl}_2/\text{Ar}/\text{SF}_6$  mixture, produced non-reproducible results and a high roughness. These observations were attributed to the redeposition of etch by-products (like  $\text{SiOCl}_x$ ) on the sample surface. It induces a micro-masking effect which generates a high roughness and leads to reproducibility issues. The so-called APETi (Alternated Process for the deep Etching of Titanium) process has been developed to prevent this roughness and increase the reproducibility. An average etch rate of  $1.4 \mu\text{m}\cdot\text{min}^{-1}$  has been achieved with reproducible features.

Comparative experiments have started on a second ICP reactor which enables higher etch rates due to a higher self-bias voltage and higher density species. The substrate holder temperature can also be higher, which should help to enhance chemical etching processes with a fluorine chemistry.

6:00pm **PS+AS+SS-WeA12 Particle Transport with Wafer Potential Controlled by Dipole Electrostatic Chuck Electrodes**, Masaki Ishiguro, M. Sumiya, Hitachi High-Technologies Corp., Japan

In plasma etching for semiconductor manufacturing, it is important to prevent particle attachment on the wafer during processing to maintain high yield rate. As the device size continue to be scaled down, smaller particles should be taken care not to attach onto the wafer. It is said that 10 nm particles will be critical for semiconductor manufacturing in 2019 [1]. One important approach to prevent particle attachment on the wafer is controlling particle transport. Electrostatic force is one of the suitable forces to control particle transport. In the case that particle charge and wafer potential polarity is opposite, large number of small particles can be attracted onto the wafer. In plasma etching process, plasma on and off periods are periodically repeated. Kobayashi *et al.* revealed that in plasma on period, the particles are trapped at the plasma sheath boundary and there is a less-risk of particle attachment to the wafer [2]. It suggested that, in plasma off period, there is a large-risk of particle attachment to the wafer if the wafer and the particles have opposite charge respectively.

In this study, the relationship between particle attachment to the wafer and wafer potential in plasma off period was investigated. Particle count on the wafer was measured at different wafer potential during plasma-off period by changing voltage settings of dipole electrostatic chuck electrodes (ESC) in Ar, O<sub>2</sub> and N<sub>2</sub> plasma. In the case of negative wafer potential, particle counts increased as the plasma off time was prolonged. On the other hand, in the case of positive or 0 wafer potential, particle count was relatively low

level and it did not increase even if plasma off time was prolonged. This result suggests that, in our experimental condition, the particles charge positive during plasma off period and they are continuously generated from inner chamber wall. If the wafer has negative potential, the particles are attracted by electrostatic force. The numerical simulation result will also be shown to understand the effect of electrostatic force on small particle attachment.

In plasma on period, wafer has plasma floating potential and the potential remains on the wafer even after plasma discharge is finished. It leads to increase of particle attachment risk as mentioned above. In this time, newly developed wafer potential control sequence with ESC electrodes to reduce wafer potential during plasma off period will be reported. This sequence enables to reduce particle attachment during plasma off period.

[1] International Technology Roadmap for Semiconductors 2013.

[2] H. Kobayashi, *et al.*, IEEE trans. Semicond. Manuf., **22**, 462 (2009).

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