

Thursday Morning, November 13, 2014

Plasma Science and Technology

Room: 308 - Session PS2+TF-ThM

Atomic Layer Etching (ALE) and Low-Damage Processing

Moderator: Geun Young Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS2+TF-ThM1 Fluorocarbon Assisted Atomic Layer Etching of SiO₂ and Selectivity over Si Using Cyclic Ar/C₄F₈ Plasma, Dominik Metzler***, University of Maryland, College Park, S.U. Engelmann, R.L. Bruce, E.A. Joseph, IBM T.J. Watson Research Center, V.A. Godyak, University of Michigan, G.S. Oehrlein, University of Maryland, College Park

There is great interest in establishing directional etching methods capable of atomic scale resolution for fabrication of highly scaled electronic devices. Recently, controlled etching of SiO₂ at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of C₄F₈ molecules, and synchronized plasma-based Ar⁺ ion bombardment has been shown [1]. Controlled etching is based on deposition of a thin (~ several Å) reactive fluorocarbon (FC) layer on SiO₂ enabled by precise C₄F₈ injection. For low energy Ar⁺ ion bombardment conditions, the physical sputter rate of SiO₂ vanishes, whereas SiO₂ can be etched when FC reactants are present at the surface. In this work, plasma conditions have been characterized in real time during cyclic exposure using a Langmuir probe. Changes in plasma potential, electron density, and electron temperature are measured throughout each cycle and compared to continuous precursor addition. Continuous precursor addition has a higher C₄F₈ concentration than periodic injection. The C₄F₈ injection has a short, significant impact on the plasma properties within each cycle and a small impact for longer time scales, i.e. from cycle to cycle. Observed trends in plasma properties agree with continuous precursor addition. Additionally, this cyclic approach was used to investigate the transition from SiO₂ to Si etching employing SiO₂-Si-SiO₂ layers. Si etching and the selectivity of SiO₂ over Si is investigated as a function of FC surface coverage, ion energy (20 to 30 eV), and etch step length using *in situ* ellipsometry. Time-dependent etch and deposition rates are compared for Si and SiO₂. The etch behavior during the cyclic approach is compared to continuous precursor addition etching of SiO₂ and Si. X-ray photoelectron spectroscopy is used to investigate surface chemistry at various stages of the cyclic etching and will be reported.

The authors gratefully acknowledge financial support of this work from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

References:

[1] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, *J Vac Sci Technol A* **32**, 020603 (2014)

8:20am **PS2+TF-ThM2 Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons, Eric Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgadino, B. Jariwala, D. Lambert, S. Deshmukh**, Lam Research Corporation

As microelectronics advancements require smaller device features, masking layers are becoming thinner. Additionally, there are tighter requirements on allowable loss of films during processing. This leads to exacting requirements for etch, where a target film must be removed with very high selectivity to a mask and/or substrate film. For etching of SiO₂ or similar materials, this high selectivity is typically achieved using very polymerizing fluorocarbon-based combinations of gases. However this approach can introduce problems with etch rate loading, such that the oxide in features with larger critical dimension (CD) tends to etch more slowly due to excessive passivation.

A novel approach for oxide etching has been developed which addresses this tradeoff between selectivity and etch rate loading. The etch process is based on repeated cycles of fluorocarbon deposition and etch reaction activation, similar to the process described by Metzler et al [1]. In each cycle there are two different phases of plasma conditions in which (1) a thin film of fluorocarbon polymer is deposited and (2) the polymer film is bombarded by noble gas ions to activate the etch reaction. Under the right conditions, oxide films are incrementally etched in each cycle. This atomic layer etch approach is less susceptible to etch rate loading because under properly adjusted conditions, the oxide etch front remains clear of polymer

buildup after each cycle. Under the same conditions, polymer can build up on the mask or substrate surface with successive cycles, protecting the film and resulting in minimal loss. The process times for the deposition and activation phases of the cycle are the primary parameters for process control. A comparison of model and experiment is presented to characterize the effect of these two time parameters upon process results.

[1] Metzler, et al *JVST A* **32**, 020603 (2014).

8:40am **PS2+TF-ThM3 Electron Beam Plasma Tool for Atomic Precision Etching, Leonid Dorf, S. Rauf, M.-F. Wu, Y. Zhang, F. Tavassoli, K. Ramaswamy, K. Collins**, Applied Materials Inc.

As the node size diminishes, microelectronics fabrication progressively requires atomic layer precision, so it becomes critical to accurately control ion energy during plasma processing. Damage caused by conventional plasma technologies (capacitively or inductively coupled plasmas) is becoming unacceptable for critical etch and clean applications. Using electron sheet beam parallel to the substrate surface to produce plasma in a processing chamber provides an order of magnitude reduction in electron temperature T_e (~ 0.3 eV) and ion energy E_i (< 2 eV without applied bias) compared to conventional plasma technologies, thus making electron beam plasmas an ideal candidate for processing features at 5 nm and below. In this presentation, we report processing results for a range of advanced plasma etching applications tested using the electron beam generated low T_e plasma. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in infinite selectivity (as per high-resolution TEM images) of silicon nitride to silicon oxide and poly-silicon in fluorocarbon based chemistries. Such high selectivity can be attributed to the two phenomena: (1) at very low bias power, ion energy is sufficiently small to allow processing near the etch threshold, and (2) plasma ions and radicals in the electron beam generated plasma are produced by highly energetic (~ 2000 eV) electrons, such that the ratio between dissociation and ionization cross-sections for most gases differs considerably from that in conventional tools with chemical processes determined by 10-15 eV electrons. The latter results in weak dissociation of the fluorocarbon gas (CH₂F₂) and relatively low free fluorine concentration, which in turn leads to very low silicon etch rate. We have also investigated a nitride spacer application, in which 20 nm nitride layer deposited conformally over a silicon fin needs to be etched away to produce straight side walls for further double patterning (as one application). Our results indicate that using the electron beam plasma provides suitably small footing with a reasonably small slant angle of the shoulder, at the same time being selective to the underlying silicon layer. Accurate analysis of several time-series of TEM images allowed characterization of lateral and vertical etch processes over a range of operating conditions, such as the bias power and the beam current. Initial studies also indicate excellent loading characteristics, even at high bias power, which again can be attributed to unique chemical composition of the processing gas in the electron beam generated plasma.

9:00am **PS2+TF-ThM4 Precise Theoretical Calculation of Neutral Beam Generation Efficiency by Collision of Chlorine Against Graphite Surface, Tomohiro Kubota**, Tohoku University, Japan, N. Watanabe, S. Ohtsuka, T. Iwasaki, K. Ono, Y. Iriye, Mizuho Information & Research Institute, Japan, S. Samukawa, Tohoku University, Japan

We investigated the generation mechanism of neutral particles in high efficiency neutral beam source developed by Samukawa et al [1], by collision of positive and negative chlorine ions against graphite surface. It is already known experimentally that neutralization efficiency of negative ion (Cl⁻) is much higher than that of positive ion (Cl₂⁺) [2]. However, the mechanism has not been clarified. Recently we investigated the neutralization mechanism by using numerical simulations based on quantum mechanics [3] and succeeded in explaining higher neutralization efficiency of negative ions than positive ions.

In this study, collision process of a chlorine particle (Cl, Cl⁻, Cl₂, or Cl₂⁺) against graphite surface was simulated by calculation based on time-dependent density functional theory (TD-DFT). Neutralization efficiency was calculated from the number of the valence electrons on the particle after the collision. By using a unit cell with enough size, dispersion of electron density into vacuum was suppressed and quantitative interpretation became possible.

Also, dependence on incident angle and energy of the particle was investigated. It was found that experimental result of energy dependence of the neutralization efficiency was quantitatively reproduced by the calculation. It suggests we have achieved a precise simulation of the neutralization process.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

* **Coburn & Winters Student Award Finalist**

- [1] S. Samukawa et al., Jpn. J. Appl. Phys. **40**, L779 (2001).
 [2] S. Samukawa, Jpn. J. Appl. Phys. **45**, 2395 (2006).
 [3] N. Watanabe et al., Phys. Rev. E **65**, 036705 (2002).
 [4] <http://www.mizuho-ir.co.jp/solution/research/semiconductor/nano>
 [5] T. Kubota et al., J. Phys. D: Appl. Phys. **45**, 095202 (2012).

9:20am **PS2+TF-ThM5 Achieving One Tenth of a Nanometer Precision in Etching of SiO₂ Over Silicon: Challenges and Opportunities**, *Gottlieb Oehrlein*, University of Maryland, College Park
INVITED

We discuss use of low pressure plasma surface interaction mechanisms aimed at achieving atomic scale precision in etching materials. Using a steady-state Ar plasma in conjunction with periodic injection of a defined number of C₄F₈ molecules and synchronized plasma-based Ar⁺ ion bombardment, we have shown that one tenth of a nanometer precision in etching of SiO₂ is possible.¹ For low energy Ar⁺ ion bombardment conditions giving a maximum ion energy of about 20eV, the physical sputter rate of SiO₂ vanishes whereas for an FC-coated SiO₂ surface, chemical modifications of the SiO₂ surface take place and SiO₂ etching is initiated. Precise management of C₄F₈ supply enables control of the deposited fluorocarbon (FC) layer thickness in the 1 to several Ångstrom range. We will discuss the temporal variation of the chemically enhanced etch rate of SiO₂ for Ar⁺ ion energies below 30 eV as a function of fluorocarbon surface coverage which enables controlled removal of Ångstrom-thick SiO₂ layers per process cycle. We will also discuss silicon underlayer etch rate measurements and challenges connected with this approach.

¹ D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, J Vac Sci Technol A **32**, 020603 (2014)

* Based on collaborations with D. Metzler, C. Li, S. Engelmann, R. Bruce, E. Joseph, E. Godyak, and M. Kushner. We gratefully acknowledge funding from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

11:00am **PS2+TF-ThM10 Numerical Simulation of Atomic Layer Etch via FPS3D**, *Paul Moroz*, Tokyo Electron US Holdings

Atomic layer etching (ALE) and atomic layer deposition (ALD) are becoming more attractive processing methods primarily due to their higher control of profiles and less induced damage to materials. They require multi-step processing, with each time-step having its own chemistry, incoming fluxes, and energy distribution of species. In this work, we simulated ALE of Si by employing a cycle of two main steps: chlorination of Si surface layer by Cl₂ gas and then removal of the chlorinated layer with Ar neutral beam of low energy and narrow energy spectrum, so the sputtering of Si could be neglected. Feature scale simulator FPS3D [1,2] is well designed for the multi-step operations and allowed us to replicate main results of the corresponding experiments [3]. Each step in ALE processing was self-limiting, and we have used the same conditions and parameters as reported for the experiment. The intermediate gas-purge steps were excluded, as simulations allow instantaneous change of chemistry and fluxes, which is not possible in actual processing. We will demonstrate simulation of ALE processing with clear time resolution of chlorination and removal steps and with etch rate corresponding to experiments.

- [1] P. Moroz, IEEE Transactions of Plasma Science, 39 (11) 2804 (2011).
 [2] P. Moroz, D.J. Moroz, ECS Transactions, 50(46) 61 (2013).
 [3] J.K. Kim, et al, J. Vac. Sci. Tech. A 31, 061310 (2013).

11:20am **PS2+TF-ThM11 Low Damage Etch Residue Removal of CoFeB Material using CO/NH₃ Reactive Ion Beam for STT-MRAM Device**, *MinHwan Jeon, K.C. Yang, D.H. Yun, J.Y. Youn, G. Yeom*, Sungkyunkwan University, Republic of Korea

Spin transfer torque magnetic random access memory (STT-MRAM) is a promising candidate for the next generation memory device due to high density, nonvolatile storage, fast switching speed, etc. comparing to conventional memory devices. For the nano scale STT-MRAM device fabrication, the dry etch process is one of the critical issues due to difficulty in the formation of volatile compounds between MTJ materials such as CoFeB, CoPt, MgO, NiFe and etch gases. The MTJ materials have been etched using conventional reactive ion etching (RIE) system with noncorrosive gases such as CO/NH₃, CH₃OH so as to increase the volatile compounds. However, the relatively low etch selectivity over hard mask material and etch residue still remain on the etched pattern sidewall. In this study, reactive ion beam etching (RIBE) system has been applied to effectively remove the etch residues remaining after the main etch of CoFeB material in the conventional ICP system. The CO/NH₃ gas mixtures was also used for the removal of the etch residues on the sidewall of etched MTJ features. After the optimized RIBE, the etch residue was effectively

removed, the surface composition was restored, and the surface roughness of the etched CoFeB thin film after the etching in the RIBE system was decreased indicating the effective removal of redeposited etch residue by the RIBE. The other characteristics of CoFeB substrate after the residue removal by the RIBE were also investigated and will be reported in the presentation.

11:40am **PS2+TF-ThM12 Effects of Cryogenic Cooling on Gallium Nitride Film in Argon Plasma**, *Daisuke Ogawa, Y. Nakano, K. Nakamura*, Chubu University, Japan

We have developed the technique to reduce the damage that is induced by argon plasma to the surface of a gallium nitride (GaN) film. Our technique especially reduces the damage relating to the band gap more than 2.5 eV. Our in-situ monitoring showed that a GaN film cooled with liquid nitrogen (LN₂) has a different pattern of the damage induced by the plasma.

In order to make the in-situ monitoring of the GaN surface, we made real-time measurements with photoluminescence (PL) spectrum emitted from the GaN film. Here, the GaN film was excited with a light illumination generated from a xenon lamp passing through a 313 nm band pass filter. This configuration allows us to monitor the volume-averaged material condition from the surface to ~75 nm depth. M. Chen previously found that the ratio of the blue luminescence (BL) band over the near-band edge (NBE) band is effective to make the in-situ monitoring of the damage induced by plasma.[1] The ratio basically gets larger as the film gets more damages. However, our result showed that the ratio stayed almost constant only when the film was cooled with LN₂. This means that the damage induced by the argon plasma was likely avoided by using LN₂ cooling.

To find the effect of the cooling with LN₂, we made X-ray photoelectron spectroscopy (XPS) measurements for three samples (pristine, LN₂, and no LN₂) after the plasma exposures. We sputtered the film with argon ion beam for 3 minutes in vacuum every cycle of the XPS measurements to obtain the depth profile. The XPS spectrum from the GaN film that was exposed in argon plasma *with LN₂ cooling* was matched well with the spectrum from the pristine GaN film after the first sputtering. On the other hand, the XPS spectrum from the GaN film that was exposed in argon plasma *without LN₂ cooling* showed a chemical shift at the gallium line and a decrease at a nitrogen line. All three spectra matched well after the second sputtering. This profile indicates that the plasma-damaged layer thicker than ~30 nm was formed in the case of no LN₂ cooling. (Assumed the sputtering rate at 5 nm/min.)

Our in-situ temperature monitoring on the GaN surface that was exposed in the argon plasma showed that the temperature stayed below 150 °C with LN₂ while the temperature exceeded over 300 °C without LN₂. This is the indication that we should be able to reduce the damage by controlling the GaN film temperature during the plasma processing.

In this presentation, we will show the evolution of the PL spectrum, connecting with the surface temperature, XPS results supporting with more details.

- [1] M. Chen et al., App. Phys. Lett. 101, 071105 (2012)

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