

## Atomic Layer Etching

### Room 104-106 - Session ALE1-MoA

#### Plasma and/or Energy-enhanced ALE I

**Moderators:** Bert Ellingboe, Dublin City University, Satoshi Hamaguchi, Osaka University, Japan

**1:30pm ALE1-MoA-1 Investigation of Atomic Layer Etching Process and UV Damage for AlGaIn/GaN HEMT, Hiroyuki Fukumizu,** Toshiba Memory Corporation, Japan; *K Kanomaru,* Toshiba Corporation, Japan; *T Kikuchi,* Toshiba Corporation

**INVITED**

Gate-recess type of AlGaIn/GaN for high electron mobility transistor (HEMT) is one of the devices which can operate normally-off for high power electronics applications. This gate-recess structure demands precise control of etching depth and minimization of etching damage to AlGaIn film. In previous atomic layer etching (ALE) studies for GaN or AlGaIn, it was first reported that the surface was oxidized by O<sub>2</sub> plasma and then subsequently this surface was removed by BCl<sub>3</sub> plasma [1]. Recently, a directional type of ALE for GaN and AlGaIn films using Cl<sub>2</sub> or BCl<sub>3</sub>/Cl<sub>2</sub> plasma and Ar ion bombardment was investigated and the surface roughness of GaN film etched by ALE was more suppressed than RIE [2]. We investigated the etching process property and UV damage on AlGaIn film and compared them between ALE and conventional RIE.

AlGaIn films were etched by Cl<sub>2</sub>/Ar chemistry for RIE. In case of ALE, a modified layer was formed by exposure to Cl<sub>2</sub> plasma and then, this modified layer was removed by Ar ion bombardment. The etched surface roughness was evaluated by AFM and the surface roughness etched by RIE increased with etching. On the contrary, the surface etched by ALE showed a relatively smooth surface regardless of the etched depth. The increase of surface roughness etched by RIE is supposed to be due to lack of nitrogen of AlGaIn film, which is confirmed with XPS. To evaluate plasma induced damage, the etched surfaces were analyzed by cathode luminescence (CL). CL intensity of near band edge (NBE) of AlGaIn decreased after RIE and ALE. The degradation of NBE intensity of AlGaIn etched by ALE was more serious than RIE. This indicated that ALE process introduced higher damages on AlGaIn film than RIE. CL intensity of NBE of GaN, which was located under AlGaIn film, also decreased after RIE and ALE. This degradation etched by ALE was larger than RIE. The residual thickness of AlGaIn film was thick enough to protect the penetration of ions into GaN film underneath the AlGaIn film. From this result, it was supposed that damage of GaN film was introduced not by ions but UV photon radiation and this UV induced damage on GaN film brought by ALE was larger than RIE. This is supposed that ALE process time was longer than RIE and UV radiation amount of ALE was also larger than RIE.

[1] S. D. Burnham, K. Boutros, P. Hashimoto, C. Butler, D. W. S. Wong, M. Hu and M. Micovic, *Phys. Status Solidi C* **7**, 2010 (2010).

[2] T. Ohba, W. Yang, S. Tan, K. J. Kanarik and K. Nojiri, *Jpn. J. Appl. Phys.* **56**, 06HB06, (2017).

**2:00pm ALE1-MoA-3 Plasma-assisted Atomic Layer Etching of Si-based Dielectric Films Studied using *in situ* Surface Diagnostics, Sumit Agarwal,** *R Gasvoda,* Colorado School of Mines; *S Wang,* Lam Research Corp.; *R Bhowmick,* Colorado School of Mines; *E Hudson,* Lam Research Corp.

**INVITED**

The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for atomic layer etching (ALE) processes for a variety of materials including Si-based dielectrics such as SiN<sub>x</sub> and SiO<sub>2</sub>. Development of new ALE processes that can meet the demands for semiconductor manufacturing requires an atomistic-level understanding of the surface reaction processes. In our group, in collaboration with Lam Research Corporation, we have pioneered the use of *in situ* optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALE.

In this presentation, I will discuss the atomistic-level details of an SiO<sub>2</sub> and SiN<sub>x</sub> ALE process consisting of CF<sub>x</sub> deposition from a C<sub>4</sub>F<sub>8</sub>/Ar plasma, and an Ar plasma activation step in which the CF<sub>x</sub> film is activated, and the underlying substrates are etched. Sequential cycles of ALE of SiO<sub>2</sub> show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC to excess CF<sub>x</sub> 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<sub>x</sub> deposition onto the SiO<sub>2</sub> 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<sub>x</sub> from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions. To further control the EPC, and obtain selective etching of SiN<sub>x</sub> over SiO<sub>2</sub>, we have explored selective attachment of surface functional groups such as hydrocarbons of different chain lengths. We have demonstrated that attachment of hydrocarbons to the surface prior to the start of ALE retards the EPC.

**2:30pm ALE1-MoA-5 Silicon Atomic Layer Etching by Two-step Plasma-enhanced Atomic Layer Deposition Consisting of Oxidation and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> Formation, E Song,** Korea Institute of Materials Science, Republic of Korea; *Ji-Hye Kim,* ISAC Research Inc., Republic of Korea; *J Ahn,* Korea Maritime and Ocean University, Republic of Korea; *J Kwon,* Korea Institute of Materials Science, Republic of Korea

The process of precise silicon etching on the atomic scale was investigated by examining the formation of an (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film as an intermediate phase followed by the removal of this layer by sublimation. An amorphous (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film was formed on a Si substrate via a two-step plasma-enhanced atomic layer deposition (PEALD) process consisting of an oxidation step involving an O<sub>2</sub> plasma and a transformation step to deposit an (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film using an NH<sub>3</sub> / NF<sub>3</sub> plasma, where the deposited thin film was removed by a sublimation process. Because the thickness of the (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> thin film could be linearly controlled by altering the number of PEALD cycles, the etching depth could be successfully controlled on the sub-nanometer scale.

**2:45pm ALE1-MoA-6 Factors in Selectively Etching SiO<sub>2</sub> over Si<sub>3</sub>N<sub>4</sub> Using C<sub>4</sub>F<sub>8</sub>/Ar Atomic Layer Etching, Chad Huard, M Kushner,** University of Michigan

Atomic layer etching (ALE) using fluorocarbon gas passivation offers several benefits over conventional etching, including increased selectivity enabled by low ion energies and increased control over polymer buildup.[1,2] This polymer is important in obtaining selective etching using fluorocarbon gases. During continuous etching the passivating fluorocarbon radical fluxes are generated by the same plasma as the activating ions, creating a close coupling between polymerizing and etching fluxes. These conditions result in limited operating conditions which produce selective etching of SiO<sub>2</sub>. ALE offers a method to decouple the passivation/polymerization phase from the activating ions, enabling a new avenue to control selectivity.

In this presentation results will be discussed from a new computational model of the etching of silicon nitride and silicon dioxide by C<sub>4</sub>F<sub>8</sub> containing plasmas. This new model, developed within the Monte Carlo Feature Profile Model (MCFPM), takes into account the transport of ion energy and radical species through a finite thickness polymer capping layer, including mixing and etching processes at the interface between the polymer and the material being etched. Applications to ALE in the context of self-aligned-contacts will be discussed.

Results from this model indicate that infinite selectivity to SiO<sub>2</sub> (over Si<sub>3</sub>N<sub>4</sub>) may be achievable in a pulse-periodic steady state ALE. This selectivity is possible because SiO<sub>2</sub> consumes more polymer during etching than Si<sub>3</sub>N<sub>4</sub>. When reactions with polymer by SiO<sub>2</sub> consumes all of the polymer deposited in each passivation phase of ALE, but the polymer consumed by Si<sub>3</sub>N<sub>4</sub> is less than the amount deposited, a thick layer of polymer will form on a cycle to cycle basis on Si<sub>3</sub>N<sub>4</sub>. This thickening will eventually prevent etching of Si<sub>3</sub>N<sub>4</sub>, while SiO<sub>2</sub> continues to etch. Before reaching this state, there is a transient period where the polymer on Si<sub>3</sub>N<sub>4</sub> is not yet thick enough to prevent etching, limiting the ability of ALE to provide perfect selectivity. In this initial period, the selectivity depends on many factors, including the ALE pulse times and the ion energy during the etching phase. Since ALE is often used to manage very thin films, the physics of this transient period where a finite amount of material is etched from both SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> takes on heightened importance.

[1] D. Metzler et al., *J. Vac. Sci. Technol. A* **32**, 20603 (2014).

[2] T. Tsutsumi et al., *J. Vac. Sci. Technol. A* **35**, 01A103 (2017).

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**3:00pm ALE1-MoA-7 Bias System for Controlling Ion Energy Distributions, Dan Carter, V Brouk, H Nguyen,** Advanced Energy Industries, Inc.

Radio frequency voltage is commonly applied for generating bias in ALE and other traditional plasma processes. As device scaling drives the need for atomic precision, techniques for improving ion energy control continue

# Monday Afternoon, July 30, 2018

to evolve. While methods combining frequencies<sup>1</sup> or harmonics<sup>2</sup>, with and without phase control<sup>3</sup> and even dynamic frequency variation<sup>4</sup> have shown promise, the very nature of sine wave excitation is conflicting for achieving narrow or freely controlled Ion Energy Distributions (IEDs)<sup>5</sup>. We investigate a new power system utilizing optimized asymmetric voltage waveforms combined with a novel control system specifically designed for controlling wafer surface potential. Using this bias voltage application we evaluate the ability to directly manipulate surface bias and resulting IED's for producing single or multiple peaks with narrow or broad energy spread. We assess a metrology approach that allows the measurement of ion energy, ion current and sheath capacitance in real time. Near mono-energetic control across a wide energy range is demonstrated. Capability down to 10's of eV is shown for plasmas in the 10 to 100 mT range making this method suitable for many energy-sensitive, atomic scale plasma processes.

1. S. Shannon et al.; J. Appl. Phys. 97, 103304 (2005)
2. P. Diomedea et al.; Plasma Sources Sci. Technol. 23 (2014)
3. Y. Zhang et al.; J. Appl. Phys. 117, 233302 (2015)
4. S. Lanham et al.; J. Appl. Phys. 122, 083301 (2017)
5. E. Kawamura et al.; Plasma Sources Sci. Technol. 8 (1999)

### 3:15pm ALE1-MoA-8 Reactions of Hexafluoroacetylacetone ( hfac) and Metal Surfaces under Low-energy Ion Irradiation, Tomoko Ito, K Karahashi, S Hamaguchi, Osaka University, Japan

In recent years, atomic layer etching (ALE) by the formation of volatile organic transition-metal compounds has been expected to establish low-damage and atomically controlled etching processes for metallic thin films. Hexafluoroacetylacetone (hfac:  $\text{CHF}_3\text{COCH}_2\text{COCF}_3$ ) is one of the candidates of organic ligands that may be used for atomic layer etching of Ni and Cu. Nigg et. al. have reported that Ni organic compounds desorb from a pre-oxidized Ni surface by hfac exposure and a control of the substrate temperature [1]. For the development of a highly anisotropic etching process, it is important to understand and control surface reactions of metal with an organic compound layer under low-energy ion bombardment. Therefore, our objectives of this study are to understand surface reactions by hfac exposure to a metal surface and to clarify effects of ion-induced reactions on hfac adsorbed metal surfaces. In this study, we have developed an atomic layer process (ALP) surface analysis system which consists of two parts: a high-resolution XPS analysis chamber and an ALP reaction chamber. After reactive gas exposure to a sample in the ALP reaction chamber, the sample can be transferred to the XPS chamber without air exposure of the sample. The hfac exposure was in the range of 100 - 10000L (in the units of L: Langmuir:  $10^{-6}$  Torr  $\cdot$  s) and Ni and Cu substrates are used in this study. The substrate temperature was set at room temperature. The hfac adsorbed surfaces were irradiated by low-energy  $\text{Ar}^+$  ions (15- 50eV) and the changes in the chemical states were observed by XPS. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond breaking. It is also found that hfac adsorbed Ni-O surfaces are fluorinated by low-energy  $\text{Ar}^+$  ion bombardment.

[1] H. L. Nigg and R. I. Masel, J. Vac. Sci. Technol. A, 17, 3477 (1999).

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