Atomic Layer Etching
Room 104-106 - Session ALE2-TuM

Modeling of ALE

Moderators: Alok Ranjan, TEL Technology Center, America, LLC, Craig Huffman, Micron

10:45am **ALE2-TuM-12 The Role of Modelling in Understanding and Designing Processes for Thermal Atomic Layer Etch***, **Simon D. Elliott**,* Schrödinger, Inc., Ireland*; S Natarajan,* Tyndall National Institute, Ireland **INVITED**

Plasma-free (or so-called 'thermal') atomic layer etch (ALE) is often described as the inverse of atomic layer deposition (ALD). In this talk we discuss whether existing approaches for the atomic-scale modelling of ALD chemistries can also be applied to ALE, what new modelling approaches are being developed for ALE and what needs are still outstanding.

Examples of the successful ALE of oxides from the literature are classified into types according to their assumed mechanisms, focusing on continuous versus self-limiting reactions, on surface conversion versus ligand exchange reactions, and on redox steps. Corresponding thermodynamic and kinetic criteria are then proposed as a framework for the theoretical analysis and prediction of ALD processes. To examine the validity of this framework, energetics computed at the level of density functional theory (DFT) for the sample ALE reactions are presented and discussed. Many of the trends observed in experiment for the ALE of oxides like alumina and hafnia can thus be reproduced and understood with relatively little computational effort. The observed temperature dependence is broken down into entropy effects in individual ALE pulses. Moving beyond this simple framework, we discuss the most important reaction steps that need to be explicity modelled for a full understanding of ALE. Early results are presented, including progress towards simulating the volatility of etch by-products. Comparisons are drawn with past work on ALD. A wish-list of future modelling needs is proposed.

11:15am **ALE2-TuM-14 Physical Damage Analysis of Atomic Layer Etching of Silicon using Molecular Dynamic Simulations***, **Ryoko Sugano**, M Kurihara,* Hitachi R&D Group, Japan*; K Kuwahara,* Hitachi High-Technologies Corp., Japan*; S Hamaguchi,* Osaka University, Japan

As the device structures shrink to atomic dimensions, more precise etch processes are required with atomic-scale controllability and lower damage. Atomic layer etching (ALE) is considered to fulfill such requirements in the fabrication of next-generation 3D devices, rather than conventional reactive ion etching [1]. Anisotropic ALE can transfer the exact dimensions of mask patterns to the underlying layer. ALE is typically achieved by two sequential self-limiting surface reactions. For example, anisotropic silicon ALE (Si-ALE) was demonstrated by the use of cyclic repetitions of cryogenic adsorption of F atoms and the subsequent Ar ion irradiation [2]. Since then, various Si-ALE has been investigated with halogen gases for the Si surface modification and Ar ion bombardment for the removal of halogen-bonded Si atoms. Ar ion bombardment in a removal step, however, causes plasma induced damages even at energy below the sputtering threshold. Experiments with low-electron-temperature plasmas showed that surface damage was considerably mitigated when ion energy was less than -10 eV [3]. With an increase of the incident ion energy, both the etched depth and damage thickness increased. Hence, for a better control of anisotropic Si-ALE, the relationship between the etched depth and damage thickness must be clarified.

In this work, to obtain low-damage process conditions for anisotropic Si-ALE, we have used molecular dynamic (MD) simulations and examined the effects of adsorbed halogen species and ion energy. The Si-ALE process analyzed in this study is based on cyclic repetitions of Br or Cl adsorption and Ar ion bombardment steps. Interatomic potential functions used in the MD simulations are of Stillinger-Weber type [4]. Plasma induced damages were estimated by the structural change in the Si lattice of the underlying Si substrate. It has been found that both the damage and the halogen penetration-depths are larger in the case of Cl than in Br, presumably due to the atomic-size difference between Cl and Br. When Cl is used for adsorption, the number of desorbed $SiCl_x$ is more than twice that of $SiBr_x$ when Br is used under similar conditions. This is because the number of Si-Cl bonds in the damaged layer is much larger than that of Si-Br bonds. MD simulations have also shown that Si-ALE with Ar ion irradiation below 20 eV causes no damage in the underlying layer below 1 nm-depth from the surface in both cases of Br and Cl.

[1] K Shinoda et al., J. Phys. D **50** 194001 (2017).

[2] Y. Horiike et al., J. Vac. Sci. Technol. A **8**, 1844 (1990).

[3] L. Dorf et al., J. Phys. D **50** 274003(2017).

[4] K. Miyake et al., Jpn. J. Appl. Phys. 53, 03DD02 (2014).

11:30am **ALE2-TuM-15 Dimer Products from Ligand-Exchange Reactions During Thermal Atomic Layer Etching***, **Andrew Cavanagh**, J Clancey, S Sharma, S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential, self-limiting fluorination and ligand-exchange reactions. One example is Al_2O_3 ALE using sequential exposures of HF and $Al(CH_3)_3$. Fluorination by HF converts Al_2O_3 to AlF_3. The ligand-exchange reactions are then believed to involve transmetalation where ligands are exchanged between the surface metal fluoride (AlF_3) and the gas phase metal precursor ($Al(CH_3)_3$). The products of these transmetalation reactions have been assumed to be monomeric metal species (e.g. $AlF(CH_3)_2$). In contrast, our recent quadrupole mass spectrometry (QMS) investigations have observed very little of the monomeric $AlF(CH_3)_2$ etch product. Instead, the main etch products are dimer species in form of $AlF(CH_3)_2$-$AlF(CH_3)_2$ and $AlF(CH_3)_2$-$Al(CH_3)_3$ (see supplemental Figure S1). These dimers are formed from the monomeric $AlF(CH_3)_2$ etch product with itself and with the $Al(CH_3)_3$ metal precursor.

To understand the relative stability between monomer and dimer reaction products, calculations were performed on all possible monomers and dimers that could be produced by the $Al(CH_3)_3/AlF_3$ ligand-exchange reaction. The potential energy surface for the reaction of $Al(CH_3)_3$ and AlF_3 confirms that dimers are the preferred etch product (see supplemental Figure S2). The dimers consist of a pair of bridging ligands between the Al metal centers and four terminal ligands. The bridging ligands can be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges result in the most stable dimers while the (CH_3, CH_3) dimers result in the least stable dimers. In agreement with the QMS results, these calculations predict that the $AlF(CH_3)_2$-$AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most stable etch product.

The computational methodology has been applied to additional ligand-exchange reactions involving fluorinated Al_2O_3, Ga_2O_3 and ZrO_2 substrates and various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. In all the systems, the calculations indicate that dimeric metal species are the most stable etch products. The ligand-exchange reactions occur, but the reaction products of the ligand-exchange remain associated in dimer metal species. The calculations predict that dimer metal species should be the stable, volatile etch products observed in future QMS studies.

11:45am **ALE2-TuM-16 Molecular Dynamics Simulation of SiO_2 Atomic-layer Etching (ALE) by Fluorocarbon and Argon Plasmas***, Y Okada, M Isobe, T Ito, K Karahashi, **Satoshi 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 etching (ALE), where etching processes take place layer by layer with each step having self-limiting chemical reactions on the surface. 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 based on digital or pulsed application of fluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive fluorocarbon radicals are first supplied to a SiO_2 surface with extremely low incident energy and a thin fluorocarbon layer is deposited there. Then the surface is irradiated with low-energy Ar+ ions, which induces reactions between fluorocarbon and SiO_2, typically forming volatile SiF_x and CO atoms, and the SiO_2 surface is etched until fluorocarbon on the substrate is essentially exhausted. In MD simulation, we have found that the actual reactions are not as simple as described above. In the Ar+ ion irradiation step, preferential sputtering of O atoms occurs even at small ion incident energy, which makes the surface more Si rich and also promotes the formation of Si-C bonds in the presence of a deposited fluorocarbon layer. C atoms bonded with Si are hard to remove by low-energy Ar+ ion irradiation and C tends to accumulate as fluorocarbon deposition steps are repeated, which may eventually lead to a complete etch stop and carbon deposition. On the other hand, a small amount of oxygen added to Ar+ ion irradiation steps can contribute to more efficient removal of carbon from the surface and also supplement the loss of oxygen due to low-energy ion bombardment. The physical sputtering yield of SiO_x is lower when its oxygen content is closer to stoichiometric SiO_2, so addition of a small amount of oxygen can also help self-limit the physical sputtering in the Ar+ ion irradiation step.

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