Atomic Layer Etching
Room Regency Ballroom A-C - Session ALE2-TuA
Modeling & Instrumentation II

Moderators: Dmitry Suyatin, Lund University, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

4:00pm **ALE2-TuA-11 First-principles Understanding of Atomic Layer Etching of Silicon Nitride using Hydrofluorocarbons***, **Gyeong Hwang**, E Cheng,* University of Texas at Austin*; S Sridhar,* TEL Technology Center, America*; P Ventzek, A Ranjan,* Tokyo Electron America Inc.

The removal of thin layers of material with atomic-scale precision and spatial control (area selectivity) is critical for advanced device fabrication, making atomic layer etching (ALE) more attractive due to its ability to tightly control etch rates and to achieve wafer scale uniformity without physical damage. While ALE processes have been widely used to remove Si, Ge, compound semiconductors, and various oxides, only a few studies on ALE of Si_3N_4 films have been reported despite its technological importance. Recent experimental investigations have demonstrated that ALE of Si_3N_4 can be achieved via sequential exposure of hydrogen and fluorinated plasma or a cyclic process involving two alternating CH_3F gas adsorption and Ar^+ bombardment steps. Both methods are avenues for area selective etch and isotropy control. However, the fundamental mechanisms by which the etching occurs are poorly understood. In this talk, we will present our recent findings regarding underlying mechanisms leading to facile ALE of Si_3N_4 using hydrofluorocarbons, based on periodic density functional theory calculations. Our study highlights the important role of adsorbates and surface functional groups. For CH_3F chemisorption on a N-rich Si_3N_4 surface, we have found a trimolecular process to be the thermodynamically most favorable pathway for initiation of the process, consisting of a nucleophilic attack of a primary amine site, if available, on CH_3F, followed by a stabilization of the fluoride leaving group by an adjacent primary amine site. While this mechanism as is has a relatively high activation energy (~0.9 eV), the presence of products from other reactions on the surface such as HF, F^-, and H^+ have been demonstrated to lower this activation energy significantly. Furthermore, we find that it is not the methylation of the surface that facilitates etching, but rather the production of H^+/F^- that helps facilitate formation of volatile N-containing species and Si-F bonds. More importantly, our study also suggests that the surface reaction mechanism responsible for Si_3N_4 ALE may be altered when CH_3F is replaced by CHF_3 or CF_4.

4:15pm **ALE2-TuA-12 An Extended Knudsen Diffusion Model for Aspect Ratio Dependent Atomic Layer Etching***, **Luiz Felipe Aguinsky**, P Manstetten,* TU Wien, Austria*; A Hössinger,* Silvaco Europe Ltd., UK*; S Selberherr, J Weinbub,* TU Wien, Austria

Atomic layer etching (ALE) is a fundamental part of semiconductor processing as device critical dimensions must be controlled to the order of nanometers [1]. One known issue in ALE, as in other etching processes, is aspect ratio dependent etching (ARDE) [2], which is the reduction of etch rates as the aspect ratio of a feature increases. One of the mechanisms linked to ARDE is the depletion of neutral species towards the bottom of a feature. This phenomenon has been investigated using a three-dimensional Monte Carlo method [3]. However, this method requires a complex setup and it is computationally expensive. For deposition processes, Knudsen diffusion [4] models provide analytical results and are actively developed. These models have been used for estimating surface parameters in some atomic layer deposition processes [5]. The Knudsen diffusion approach arises from physical considerations to the mass balance at each volume element. Alternatively, given isotropic reflections and particle source, the fluxes can be calculated exactly over the whole domain via the radiosity equation [6]. The radiosity approach requires the assembly and inversion of a matrix describing the exchanges, being notably unsuitable for low sticking regimes.

We propose a model extending the standard deposition Knudsen diffusion approach by including the direct flux from a particle source and a geometric factor to enable a more rigorous picture of ARDE in ALE. The inclusion of the direct flux is motivated by the radiosity equation, while avoiding the costly matrix inversion step. The geometric factor enables a more accurate description of the geometry by integrating over the whole feature at each volume element. We compare our extended Knudsen diffusion model against a reference radiosity model [6], achieving good agreement. Our results highlight one shortcoming of the standard Knudsen diffusion model: The flux near the bottom of a high aspect ratio feature is underestimated. We also show that the geometric factor describes the particle transport more accurately near the extremities of finite cylinders.

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs and the National Foundation for Research, Technology and Development is gratefully acknowledged.

[1] K. Ishikawa et al., Jpn. J. Appl. Phys. **56**, 06HA02 (2017).

[2] C.G.N. Lee et al., J. Phys. D: Appl. Phys. **47**, 273001 (2014).

[3] C. Huard et al., J. Vac. Sci. Technol. A **35**, 05C301 (2017).

[4] A. Yanguas-Gil, Growth and Transport in Nanostructured Materials (Springer, 2017).

[5] M. Ylilammi et al., J. Appl. Phys. **123**, 205301 (2018).

[6] P. Manstetten et al., Solid-State Electron. **128**, 141 (2017).

4:30pm **ALE2-TuA-13 Thermodynamics-Based Screening Approach for Atomic Layer Etching***, **Nagraj Kulkarni**,* Unaffiliated

A thermodynamics-based approach for screening directional or thermal Atomic Layer Etching (ALE) processes is discussed for the purpose of achieving high synergies close to unity. The Ta-Cl system was selected as a test case for this analysis. Reaction equilibria for over 30 condensed-gas species were computed from available thermodynamic data in this system. Suitable process conditions for the formation of stable reaction products or compounds and the corresponding partial pressures of known gas species were first obtained with the aid of volatility diagrams that were calculated using thermodynamic data for all known solid-gas reactions. For optimum conditions during the first stage of a typical ALE process (passivation step), the selection of suitable metal-gas compound/s that have very low vapor pressures and hence negligibly low etch rates was made. For optimum conditions during the second stage (inert ion sputtering) of a directional ALE process, an assessment of the potential for selective sputtering of the selected compound/s relative to the base metal was made from knowledge of the surface binding energies of the base metal and relevant compound/s that are usually considered to be the enthalpy changes of the relevant solid-gas sputtering reactions at room temperature. In the case of an isotropic, thermal ALE process, the selection of suitable temperatures for the direct volatilization of the reaction product layer during the second stage of ALE is also discussed.

4:45pm **ALE2-TuA-14 Always in Competition: Self-limiting Versus Continuous Reactions in ALD and ALEt***, **Simon D. Elliott**,* Schrödinger, Inc.*; S Natarajan, R Mullins, M Nolan,* Tyndall National Institute, Ireland*; A Cano, J Clancey, S George,* University of Colorado - Boulder

One of the main challenges in designing novel atomic layer deposition (ALD) and atomic layer etch (ALEt) processes is to ensure the self-limiting (SL) nature of reactions during the individual precursor pulses at the target temperature of interest. It is important to establish a SL temperature window to ensure that the precursors will not produce chemical vapour deposition (CVD) or chemical vapour etching (CVE). To that end, we have developed a first principles based computational methodology to study the competition between continuous and SL reactions when a material surface is exposed to precursor gases.

ALEt processes for oxides have been reported using sequential fluorination by HF and ligand exchange reactions at elevated temperatures.[1] Herein, we investigate the nature of the HF pulse when treating a range of materials including B_2O_3, TiO_2, HfO_2, ZrO_2, Al_2O_3 and TiN by comparing the free energy profiles of the potential CVE and SL reactions computed with density functional theory (DFT). In general, elevated temperatures favour CVE of these materials, whereas fluorination of the surface is self-limiting at lower temperatures. HF was computed to continuously etch B_2O_3 and TiO_2 even at temperatures below 100°C by forming volatile fluorides. This is in good agreement with experimental FTIR, where the onset of continuous etching of TiO_2 by HF was found at 80°C – 90°C and where etching of B_2O_3 proceeded even more rapidly than that of TiO_2. However, in another example, HF is predicted to preferably etch HfO_2 above 160°C, whereas experiment[1] shows the process to be still self-limiting at 200°C. Therefore, this simple thermodynamic analysis, which does not include reaction kinetics, is only able to provide a lower threshold temperature at which a CVE reaction may become favourable, subject to overcoming any kinetic barrier. We also computed that Al_2O_3 resists continuous etching up to 340°C while TiN can not be etched until temperatures exceed 1300°C.

This methodology is also used to understand the competing CVD and SL reactions in the ALD of Ru using the RuO_4 precursor and H_2.[2] The DFT

calculations show that RuO_4 undergoes an SL decomposition into RuO_2 on electron-rich surfaces and that this is in competition with CVD.

These examples illustrate that this relatively quick computational approach can be effectively used to screen candidate precursor molecules to be selected for material processing.

1. Y. Lee et al., *Chem. Mater.28*, 7657-7665 (2016).

2. M. M. Minjauw et al., *J. Mater. Chem. C3*, 132-137 (2015).

5:00pm **ALE2-TuA-15 Variation of Etched Depth per Cycle and Removal of Reactive Species in Atomic-Layer Etching (ALE) : Molecular Dynamics Study**, ***Satoshi Hamaguchi,*** *E Tinacba, S Shigeno, Y Okada, M Isobe, T Ito, K Karahashi,* Osaka University, Japan

Alternating application of reactive species from a plasma with no bias energy and Ar plasma with low bias energy to a Si-based film (such as Si, SiO2, and SiN) can cause atomic layer etching (ALE) of its surface. In this process, the initial application of reactive species to the surface will leave a sufficient number of reactive species (e.g., Cl atoms) bonded with the surface atoms (e.g., Si, forming Si-Cl bonds) and, in the second step where low-energy Ar+ ions irradiate the surface, a thin mixed layer of the reactive species and surface atoms is formed and volatile molecules (e.g., SiCl4) desorb from the surface. Since the incident energy of Ar+ is too low to physically sputter surface atoms, etching or desorption of volatile species ends as soon as reactive species are exhausted from the surface - even if Ar+ ions continue to bombard the surface with low incident energy. This self-limited etched depth of a single cycle (i.e., application of reactive species and application of low-energy ions) allows “nearly” layer-by-layer etching of the material surface. At the end of each cycle, where self-limited etching takes place, some reactive species tend to remain on the surface or in the subsurface region, causing surface roughness. Depending on how deep such reactive species diffuse into the subsurface region or how thick the formed mixed layer becomes, the etched depth per cycle changes. In this study, etched depth per cycle and remaining reactive species are discussed based on the results of molecular dynamics (MD) simulation of single cycles of various ALE processes. Example considered here include Si ALE by fluorine reactions, SiO2 ALE by fluorocarbon reactions,

And SiN etching by hydrofluorocarbon or hydrogen reactions.

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