

Atomic Layer Etching

Room Baekeland - Session ALE1-TuA

In situ Studies, Mechanisms and Modeling of ALE

Moderators: Sumit Agarwal, Colorado School of Mines, Dmitry Suyatin, Lund University

1:30pm **ALE1-TuA-1 Surface Reaction Mechanisms by Metal-Organic Compound Formations in Atomic Layer Etching Processes, Tomoko Ito**, Osaka University, Japan; *A. Basher*, King Abdullah University of Science and Technology, Saudi Arabia; *K. Karahashi*, *S. Hamaguchi*, Osaka University, Japan

INVITED

Transition metals are known as hard-to-etch materials for reactive ion etching (RIE). In recent years, atomic layer etching (ALE) based on the formation of highly volatile metal compounds from surface metals and organic gases has been proposed as atomically controlled and damage-less etching for transition metals [1]. In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, various volatile metal-organic compounds such as β -diketonates (such as nickel(II) acetylacetonate: $\text{Ni}(\text{acac})_2$ and Nickel(II) hexafluoroacetylacetonate: $\text{Ni}(\text{hfac})_2$) and metallocenes (such as nickelocene) are known as metal precursors. The metal ALE process mentioned above, where volatile metal β -keto enolates or metallocenes are formed on a metal surface, may be considered as a reverse process of such ALD. The development of new ALE processes for various transition metals requires a better understanding of surface reactions of metals with gas-phase organic molecules. Therefore, the goals of this study are to understand how organic compounds adsorb on transition metal surfaces and react with transition metal surfaces. Moreover, we want to clarify the mechanisms of the formation of volatile metal compounds and their desorption processes. In this study, we focused on the surface reactions of Ni and Co with hexafluoroacetylacetonate (hfacH) and acetylacetonate (acacH) gases, which were analyzed experimentally with the Atomic Layer Process (ALP) Analysis System and theoretically with density functional theory (DFT) calculations [2,3]. The ALP Analysis System, which consists of an *in situ* high-resolution X-ray Photoelectron Spectroscopy (XPS) system and an ALP reaction chamber, allowed us to examine the chemical compositions and bond formation of the metal and metal oxide surfaces on which hfacH or acacH molecules adsorbed. ALE processes of Ni and Co films were also confirmed experimentally with oxidation and hfacH exposure at elevated temperatures. DFT calculations also clarified the mechanisms of self-limiting reactions in thermal ALE of Ni with hfacH and acacH exposure, which were found to be consistent with experimental observations.

[1] J. Zhao, et. al., Appl. Surf. Sci. 455, 438 (2018).

[2] A. H. Basher, et al., J. Vac. Sci. Technol. A 38, 052602 (2020).

[3] A. H. Basher, et al., Jpn. J. Appl. Phys. 59, 090905 (2020).

2:00pm **ALE1-TuA-3 Atomic Layer Etching of Al_2O_3 on Metallic Substrates Using *in situ* Auger Electron Spectroscopy, Andrew Cavanagh, S. George**, University of Colorado at Boulder

Ultra-sensitive techniques are required to observe the final cycles of atomic layer etching (ALE) as the etch process becomes a surface cleaning procedure at the interface of the film and the substrate/etch stop. With a sensitivity of $\sim 1\%$ of a monolayer, Auger electron spectroscopy (AES) is well suited for measuring the removal of a film with ALE. AES peak height ratios of the film and the underlying substrate provide a quantitative measurement of the film thickness during ALE. The peak height ratios were evaluated using a model developed by Holloway.

ALE of Al_2O_3 was performed using hydrofluoric acid (HF, 10% solution in pyridine) and trimethylaluminum (TMA). The sample stack was $\text{Al}_2\text{O}_3/\text{Au}/\text{Y}_2\text{O}_3$ (adhesion layer) / SiO_2 (native oxide)/Si. The gold underlayer provided a chemically inert, highly conductive interface ideal for AES studies. AES measurements were conducted periodically throughout the etch process and used to determine the thickness of the Al_2O_3 film. The instrument used for these measurements allowed for the transfer of the sample from an ALE process chamber (~ 1 Torr) to the ultra-high vacuum analysis chamber used for AES (10^{-10} Torr) without exposure to atmosphere.

The reduction in the aluminum and oxygen AES peak intensities from the Al_2O_3 film and the increase in the gold substrate peak intensity was observed as a function of the number of ALE cycles at 250°C (Figure 1). As monitored by AES, the etch per cycle of Al_2O_3 with HF and TMA at 250 °C

was determined to be $0.3 \text{ \AA} \cdot \text{cycle}^{-1}$. At the $\text{Al}_2\text{O}_3 - \text{Au}$ interface, once the Al_2O_3 film had been nominally removed, Al and O atoms remained on the surface. Additional cycles of HF and TMA continued to remove this material, effectively cleaning the substrate surface (Figure 2). AES observations for the Al_2O_3 ALE process on Au substrates will be presented for different reaction conditions.

2:15pm **ALE1-TuA-4 In-situ Optical Emission Spectroscopy as a Tool to Characterize Cyclic Quasi-Atomic Layer Etching, Yoana Ilarionova**, Lund University, Sweden; *M. Karimi*, Alix Labs, Sweden; *D. Lishan*, *D. Geerapuram*, Plasma-Therm LLC; *R. Jafari Jam*, *D. Suyatin*, *J. Sundqvist*, AlixLabs, Sweden; *I. Maximov*, Lund University, Sweden

Atomic layer etching (ALE) is one of the most advanced etching processes today, which enables atomic precision in a cyclic etching, where the material is removed layer-by-layer. In an implementation of ALE, a monolayer of reactive gas is chemisorbed on the surface of the etched material providing surface activation. The activated surface is then removed by plasma - usually by low-energy ions extracted from the discharge. They provide sufficient energy to remove only the reaction products leaving inactivated material.

In practice the ions may contribute to the physical sputtering of the etched material, thus increasing the total etch rate above the values of pure ALE. The residual reactive gas in the reaction chamber can dissociate in the plasma and also increase the etch rate. This etching mode can be defined as a "quasi-ALE" with contributions from the sputtering and reactive ion etching (RIE). To realize a "real or pure" ALE regime with negligibly small unwanted effects, careful optimization of process conditions is necessary. In the current work, we apply optical emission spectroscopy (OES) in a quasi-ALE cyclic process to monitor the relative concentration of active Cl_2 species in the chamber and relate it to the observed etch rate of Si.

In our experiments, we used a commercially available Inductively Coupled Plasma RIE Takachi™ tool (Plasma-Therm LLC, USA) with Cl_2 and Ar as process gases. Silicon samples were patterned with Talbot displacement lithography to produce specimens with resist masks. The etch rates were measured after the samples were cleaved and inspected with a scanning electron microscope. The OES measurements were performed in the wavelength range 191 - 887 nm using an in-situ spectrometer. The etch cycle included the following steps: injection of molecular Cl_2 , purging with Ar to remove the excess chlorine, Ar-plasma etching and purging again.

Here we present a correlation between the average Si etch rate per cycle (EPC, determined by the etch depth divided by the number of cycles) and the intensity of the 257 nm Cl-peak as measured by the OES. The peak is generated during the Ar plasma step due to the presence of excess Cl_2 . The experiments show that both the EPC and the Cl-peak increase with the increase of injection time and follow the same trend. A dependence between the EPC and the OES intensity is also observed. The measured EPC of 6.3-8.2 Å exceeds the expected EPC for pure ALE, indicating an excess of Cl_2 . This indicates that the purging time affects the amount of residual Cl_2 . Finally, we also discuss other applications of OES in the optimization of a quasi-ALE process.

2:30pm **ALE1-TuA-5 Atomic Layer Etching of CAR/SOG in EUV Patterning of 300 Mm Wafers - Selectivity and Roughness Mechanisms, François Loyer**, P. Bezar, R. Blanc, F. Lazzarino, S. De Gendt, IMEC, Belgium

Future technological nodes (N3 and below) will see further shrinking of not only the pattern dimensions, but of photoresist film-thickness as well. The etching of Spin-On-Glass (SOG) using a Chemically-amplified-resist (CAR) mask following lithography is strongly affected by this trend as the selectivity of the conventional etch processes will soon no longer be sufficient. Furthermore, roughness reduction techniques as we know them will also be challenged as they typically consume some of the already-meagre CAR budget. Therefore, the reactive-ion-etching - based atomic layer etching (RIE-ALE) of SOG with a CAR mask is investigated as a softer and more selective alternative to conventional RIE. The RIE-ALE of SOG and the transfer into underlying hard mask have been demonstrated on coupons as well as on 300 mm full wafers, highlighting a strong increase of selectivity compared to RIE in coupons. However, the ALE process also yielded a higher roughness than RIE which doesn't meet the requirements for EUV patterning.

An investigation of the mechanisms leading to this improvement of selectivity together with the deterioration of the roughness is provided, highlighting the lack of chemical contrast due to the reactivity of the fluorocarbons, the role of redeposition mechanisms and the importance of interfacial interactions. Indeed, the mechanisms of fluorination during the patterning process become essential to understand and optimize the

processes, as the very thin layers become deeply modified within their bulk.

The selectivity observed on patterned wafers can be explained by redeposition mechanisms, as the fluorocarbon-mixed layers formed in ALE are sputtered and redeposit on the CAR mask. Redeposition mechanisms are not suitable for an optimal roughness control as their statistical distribution leads to an increase of the LER and LWR. Moreover, the surface properties of both the CAR photoresist and SOG underlayer being deeply altered during the fluorination, the formation of complex interfaces as the ALE process occurs are expected to occur which induce further stress – hence roughness – within the layers. Surface free energy (SFE) measurements highlight the evolution of the dispersive (*i.e.*, London force) and polar (*i.e.*, Coulomb force) components of the layers during the patterning. Those interactions driving the gas to solid interactions before the formation of the mixed layer and the interface with the bulk, they provide valuable information on the potential stress within the stack.

2:45pm ALE1-TuA-6 Ab Initio Calculations on the Thermal Atomic Layer Etching of Copper, Xiao Hu, J. Schuster, Chemnitz University of Technology, Fraunhofer Institute for Electronic Nano Systems, Center for Materials, Architectures and Integration of Nanomembranes (MAIN), Research Fab Microelectronics Germany., Germany

Copper interconnects are widely used in ULSI circuits due to their low resistivity and superior resistance to electromigration. Traditionally, the patterning of copper and barrier metals in the damascene process relies on chemical mechanical planarization (CMP), which may cause damages to fragile low-k interlayer dielectrics. Thermal atomic layer etching (ALE) is an emerging technique that uses sequential, self-limiting reactions to remove materials with high selectivity [1]. Thermal ALE is being considered an alternative to CMP as a final material removal step in the copper damascene process [2]. Recently, the thermal ALE of copper was demonstrated using O₂ or O₃ and H(hfac) (hexafluoroacetylacetonate) as the reactants [3]. Besides the oxidation mechanism, metal ALE can also be achieved through halogenation and ligand volatilization. For example, Co ALE has been demonstrated using Cl₂ and H(hfac) as the reactants [4]. In this work, theoretical calculations based on density functional theory (DFT) were performed to explore the possibility of Cu ALE through halogenation and ligand volatilization.

Using ab initio thermodynamic calculations, we have compared the Gibbs free energies of the reactions between H(hfac) and CuO, Cu₂O, and CuCl₂, as shown in Figure 1. It is found that the CuO + H(hfac) and Cu₂O + H(hfac) reactions are exothermic and have negative ΔG values between 300 K and 700 K. In contrast, the CuCl₂ + H(hfac) reactions are only favorable at temperatures higher than 425 K. Thermodynamic calculations suggest that a higher reaction temperature is required for Cu ALE using Cl₂ and H(hfac) as the reactants. In the next, we performed DFT calculations to investigate the elementary reaction steps of Cu ALE. During the Cl₂ exposure, the Cu surface is chlorinated to CuCl₂. During the H(hfac) exposure, the surface CuCl₂ is converted to gaseous HCl and Cu(hfac)₂. The surface reaction between CuCl₂ and H(hfac) consists of several elementary steps including H(acac) dissociation, hydrogen diffusion, Cu(hfac)₂ formation, and HCl and Cu(hfac)₂ desorption. The rate-limiting step is found to be the desorption of HCl and Cu(hfac)₂, with an activation energy of about 1.7 eV. Lastly, we focused on the computational evaluation of ligands for CuCl₂ volatilization. Various candidate ligands including acac, NacNac, dki, pyrim, dmap, and amd have been considered in this work.

[1] George, S.M. et al., ACS Nano, 2016, 10, 4889-4894. [2] Carver, C.T. et al., ECS J. Solid State Sci. Technol., 2015, 4, N5005-N5009. [3] Mohimi, E. et al., ECS J. Solid State Sci. Technol., 2018, 7, P491-P495. [4] Konh, M. et al., J. Vac. Sci. Technol. A, 2019, 37, 021004.

3:00pm ALE1-TuA-7 Transport and Reaction Kinetics Modelling of Thermal ALE in High Aspect Ratio Hafnium Oxide Structures, Andreas Fischer, D. Mui, A. Routzahn, R. Gasvoda, J. Sims, T. Lill, Lam Research Corporation

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing 5 and 3 nm devices in the semiconductor industry. Critically, stacked chip architectures such as 3D NAND and 3D DRAM require conformal isotropic etching to remove material such as HfO₂ in hard-to-reach locations with aspect ratios that can be >50. To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack. In this work, we have modelled the reaction kinetics and transport processes of reactants and by-products during a cyclical ligand exchange-based ALE process. This ALE process

consists of two steps: a fluorination step, followed by a fluorine-to-chlorine ligand exchange-based removal step. Experimental data revealed that the fluorine dosing during the fluorination step was predominantly responsible for controlling the etch rate of the ALE process but had only a minimal impact on the etch profile inside these holes. The ligand exchange dosing, on the other hand, predominantly controlled the etch profile (depth loading) with equal etch rates top-to-bottom obtained when the step was operated close to saturation. Our model predicts, in agreement with the experiment, that adsorption and reaction rates during fluorination on HfO₂ surfaces are significantly slower than transport times inside these deep holes leading to essentially flat fluorination profiles even if the fluorination step is not operated in saturation mode. In contrast, transport rates with the ligand exchange molecule are slow in comparison but adsorption and ligand exchange rates with the fluorinated hafnium appear to be significantly higher than for fluorine during the fluorination step. Slow transport in combination with high surface reaction rates for the ligand exchange step led to an etch rate that was dependent on aspect ratio (feature depth) in processes that used sub-saturation exposures.

3:15pm ALE1-TuA-8 Damage Formation in the Underlying Silicon after the Removal of Silicon Nitride by Atomic Layer Etching: A Molecular Dynamics Study, Jomar Tercero, Osaka University, Japan; A. Hirata, Sony Semiconductor Solutions Corporation, Japan; M. Isobe, K. Karahashi, Osaka University, Japan; M. Fukasawa, Sony Semiconductor Solutions Corporation, Japan; S. Hamaguchi, Osaka University, Japan

Molecular dynamics simulations were performed for a better understanding of the formation mechanisms and extent of damage in the underlying silicon (Si) material when a silicon nitride (Si₃N₄) layer above it was removed by atomic layer etching (ALE). ALE is an etching technique known to remove a surface layer of a material with atomic-level control and precision. On account of this, extensive research was focused on devising ways to obtain a uniform and stable etching performance with good selectivity to other materials, to cope with high demand from the semiconductor industry. However, though ALE is known to etch a very thin layer at a time, problems such as over-etching or damage on the underlying material layer might still occur during the fabrication [1]. Therefore, in this study, ALE of Si₃N₄ formed on a Si surface was examined, with the use of molecular dynamics simulation. As in experiments, the surface modification step was performed with the adsorption of CH₂F radicals, and the removal step was performed with the irradiation of the modified layer with Ar ions. To assist the removal of the remaining HFC species, O ions were introduced after the removal step. Recent experimental observations showed that the HFC species penetrated deeply into the underlying Si during the first ALE cycle [2]. Our simulation showed that the HFC and Si₃N₄ species penetrated the underlying Si material to a depth of around 4 nm, in the removal step with 300 eV of Ar ion incident energy. The higher the Ar ion incident energy was, the deeper penetration depths of the HFC were observed. Moreover, the bond distributions showed that those penetrated species formed chemical bonding with surrounding Si atoms. As a consequence, the extent of damage or the thickness of the amorphized Si layer was also found to be around 4 nm. The results also showed that physical sputtering tended to dominate the ALE process as the Ar ion incident energy increased, where a large number of monoatomic species left the surface during the removal step. The results suggest that the Ar ion incident energy has a significant contribution to the damage generation in the underlying Si material.

References

1. Tinacba, E., Isobe, M., and Hamaguchi, S., *JVST A39*, 042603 (2021).
2. Hirata, A., Fukasawa, M., Kugimiya, K., Karahashi, K., Hamaguchi, S., Hagimoto, S., and Iwamoto, H., *DPS 2021* (2021).

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