Live Session
Room Live - Session LI3-WeM

Technical & Poster Sessions: Wednesday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Jean-François de Marneffe, IMEC

10:00am **LI3-WeM-7 Welcome & Introduction**, ***Christophe Detavernier***, *J Dendooven,* Ghent University, Belgium; *P Poodt,* TNO/Holst Center, Netherlands; *E Kessels,* Eindhoven University of Technology, Netherlands; *H Knoops,* Oxford Instruments Plasma Technology, Netherlands; *J de Marneffe,* IMEC, Belgium

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10:15am **LI3-WeM-8 Surface Reactions Between Metals and Diketone induced by Gas Cluster Ion Bombardments**, ***Noriaki Toyoda***, *K Uematsu,* University of Hyogo, Japan **INVITED**

Gas cluster ion beams (GCIB) are aggregates of several thousands of gaseous atoms or molecules. Since the thousands of low-energy (several eV) atoms bombard a surface at the same time and the same position, the bombarded area experiences transient high-temperature and high-pressure conditions, which enhance sputtering of atoms or molecules. By using these characteristics, GCIB is now widely used for surface analysis tools in XPS or SIMS system. In recent years, we are investigating the feasibility of GCIB as energetic ions to enhance the surface reactions between adsorbed molecules and target atoms. We have reported ALE process using GCIB for transition metals (Cu and Ni) with diketone (acetylacetone and hexafluoroacetone). We separated each etching step as following; (1) adsorption of diketone molecules on metal oxide, (2) evacuation of residual vapor, (3) irradiation of O_2-GCIB to remove metal oxide. By using 5 keV O_2-GCIB (~ 2eV/molecules), thin layer of nickel oxide with adsorbed acetylacetone is removed. There is no physical sputtering at this energy region, which realizes self-limiting ALE process. From in-situ XPS study, Ni oxide with adsorbed diketone molecules can be removed by Ar-GCIB irradiation. It means that other oxidation method can be used to form metal oxide, and Ar-GCIB can be used for the removal steps. In this talk, we will report surface reactions between metals and diketone induced by gas cluster ion bombardments, and etching characteristics of various metals using GCIB irradiation and diketone.

10:45am **LI3-WeM-10 ALE 2020 Best Student Paper Award Talk: Isotropic Plasma ALE of Al_2O_3 using SF_6 Plasma and TMA**, ***Nicholas Chittock***, *M Vos, A Mackus,* Eindhoven University of Technology, Netherlands; *H Knoops,* Oxford Instruments Plasma Technology, Netherlands; *E Kessels,* Eindhoven University of Technology, Netherlands

Isotropic ALE is typically achieved using thermal chemistries, while plasma ALE processes are generally anisotropic in nature due to directional ions generated by the plasma. In this work, a plasma ALE process for isotropic etching of Al_2O_3 is introduced which involves SF_6 plasma exposure and TMA dosing. This process demonstrates that a fluorine containing plasma can serve as a viable co-reactant for ALE, and that plasmas can also be utilized for isotropic ALE.

From Fourier transform infrared spectroscopy (FTIR) analysis it was deduced that the SF_6 plasma step eliminates surface methyl groups while also fluorinating the surface. This fluorinated region is then removed by dosing TMA, similar to the pathway for the thermal HF/TMA ALE process.[1-5] A decrease in the Al-O IR absorbance peak for increasing ALE cycles indicates that the process is effective for etching Al_2O_3.

Self-limiting ALE behavior of this etch process was confirmed by measuring saturation curves for SF_6 plasma exposure and TMA dosing using in-situ spectroscopic ellipsometry, yielding an etch per cycle (EPC) of 3.1 Å/cycle at a substrate temperature of 260 ˚C. Higher EPC values than previously observed in the literature for thermal ALE of Al_2O_3 were obtained over the investigated substrate temperature range of 155 – 285 ˚C.[1-5] Furthermore a significant EPC of 0.83 Å/cycle was already achievable at the low substrate temperature of 185 ˚C. Performing multiple doses of only one half-cycle does not lead to observable etching of either Al_2O_3 or HfO_2 surfaces, while the complete ALE cycle was effective for etching both materials, thereby demonstrating the synergy of the ALE process. The measured EPC of HfO_2 ALE is 1.1 Å/cycle using the SF_6 plasma TMA process, which is higher than previously reported for a similar thermal HF/TMA process.[6] The isotropic nature of the plasma ALE process was demonstrated by transmission electron microscopy (TEM) analysis of 3D trench structures, with the Al_2O_3 thickness on Si trench structures being analyzed before and after etching. This work highlights that the use of plasmas allows for extension of the operating space for isotropic ALE by offering lower temperatures, higher EPC values and alternative plasma co-reactants.

1. Lee, Y., et al., Chem. of Mater. , **28**, pp.2994 (2016)

2. Cano, A., et al., J. of Phys. Chem. C ***123*** , 10346 (2019)

3. DuMont, J., et al., J. of Chem. Phys , **146**, 052819 (2017)

4. Zywotko, D., et al., JVST A , **36**, 061508 (2018)

5. Hennessy, J., et al., JVST A , **35**, 041512 (2017)

6. Lee, Y., et al., Chem of Mater. **28**, pp.7657 (2016)

11:15am **LI3-WeM-12 Monolayer Lithography: Exploiting Inhibition Contrast from the Extreme Ultraviolet Irradiation of Organic Monolayers for Area Selective Depositions**, ***Rudy Wojtecki***, IBM Research - Almaden **INVITED**

The enablement and miniaturization of technologies, such as electronic devices, are largely dependent on patterning materials. For instance, polymer resists can be used to create a broad range of desired feature geometries that continue to extend the capabilities of nanoscale fabrication at a remarkable rate. The 7nm technology node, which is reliant on extreme ultraviolet exposures exposures, may still rely on chemically amplified resists (CARs) from previous technology nodes. However, at critical dimensions (CDs) and below, CARs reveal increasingly difficult challenges to achieve the resolution and line edge roughness demanded by future technology generations. These include: the low absorbance of organic polymeric materials can lead to low aerial image contrast and may require higher dose exposures that reduce throughput. An alternative bottom-up approach to patterning using an organic monolayer and subsequent area selective deposition technique that can be tuned to a positive or negative-tone image generation. The method of aerial image generation in monolayer lithography takes advantage of two processes that can be used to build contrast in image development as the sensitivity of the organic itself is not alone sufficient for high contrast imaging: (i) removal of a desired organic material after exposure and (ii) a post exposure area selective deposition. These organic materials exhibit a non-linear relationship in a subsequent area selective deposition (ASD) image development step using atomic layer deposition (ALD), a key component for the development of a high-resolution system. This approach provides a method that utilizes the thinnest possible organic material and a pattern development step that produces an effective etch mask for pattern transfer.

11:45am **LI3-WeM-14 Super-Conformal ALD of Metallic Mo Films by Simultaneous Deposition and Etch**, ***Jean-Sebastien Lehn***, EMD Performance Materials; *C Dezelah,* ASM, Finland; *J Woodruff, R Kanjolia, D Moser, T Polson,* EMD Performance Materials

Super-conformal ALD processes, where more material is deposited at the bottom of a narrow trench or via versus its top, are needed for future generations of micro-electronic devices. Standard conformal ALD processes are unable to fill a via/trench without leaving a hollow seam. Using a conformal ALD process to fill re-entrant features, where the opening is narrower compared to the features' bottom, will lead to a void. These defects result in performance and reliability problems.

Recently disclosed super-conformal ALD processes require additional steps compared to the normal ALD sequence. A bottom-up deposition process had been developed for copper, relying on catalytical iodine atoms.[1] The addition of a nitrogen-plasma based inhibiting step,[2] or of etching steps,[3] had been demonstrated as pathways to bottom-up growth. These approaches, however, lengthen the deposition process, and may lead to increased impurities.

A new simple ALD process to deposit molybdenum films only at the bottom of vias is presented here.[4] It uses only two precursors, $MoCl_5$ and CHD (2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene), a strong reducing agent active at low temperatures where H_2 is inactive. This process does not require a catalyst, a growth inhibitor, or an additional etchant. This is possible as $MoCl_5$ quickly deposits a monolayer of $MoCl_x$ while it slowly etches Molybdenum (Scheme in Figure 1). The etched Molybdenum species can also be re-deposited on available sites. The ratio between the etch and the deposition depends on the gas phase concentration of chemical species. Increasing the $MoCl_5$ dose leads to a slowly-increasing deposition rate and a rapidly-increasing etch rate; therefore the Molybdenum deposition rate shows a maximum when the $MoCl_5$ dose is varied (Fig. 2a).

When depositing Molybdenum inside vias, chemical species' concentrations vary with the depth within the via. It is therefore possible to deposit Molybdenum only at the bottom of vias – a super-conformal process (mechanism shown in Fig. 2b). Fig. 2c shows SEM/EDS of vias with Molybdenum deposited only at the bottom of vias. Molybdenum can also be selectively deposited between substrates (the deposition/etch ratio is substrate-dependent during the nucleation phase). Characterization of films grown with this new ALD process will be shared.

* EMD Performance Materials is a business of Merck KGaA, Darmstadt, Germany.

(1) Au Y. et al. J. Electrochem. Soc. **158**, D248 (2011)

(2) Lai et al. US 9748137

(3) Fu et al. US 9595466

(4) Lehn, J.-S.M. et al. WO 2018/234567 A1

(5) Klesko, J.P. et al. Chem. Mater. **27**, 4918 (2015)

12:15pm **LI3-WeM-16 Process Optimization in Atomic Layer Deposition Using Machine Learning**, *A Yanguas-Gil, S Letourneau, A Mane, N Paulson, A Lancaster,* ***Jeffrey W. Elam,*** Argonne National Laboratory

Process development and process optimization are ubiquitous, resource-intensive tasks in thin film research and development. The goal of these activities is to find the set of process parameters (e.g. temperature, pressure, and flow) that maximize film quality at minimal cost. Typically, this is accomplished by coating a substrate (e.g. a silicon wafer) under a given set of conditions, measuring the film properties ex situ, and adjusting the conditions to improve the film quality. This activity can consume significant time and resources, especially if an additional goal is to achieve uniform films across a large substrate. Process development can be accelerated and economized using in situ measurements. For instance, quartz crystal microbalance (QCM) measurements can be employed to monitor film thickness in real time as the deposition conditions are varied. However, this still requires the careful attention of a skilled operator to make informed choices based on experience and intuition. An alternative strategy is to use machine learning (ML) to analyze the QCM data in real time and adjust the growth conditions based on an algorithm. To explore this possibility, we used ML to optimize the atomic layer deposition (ALD) of Al_2O_3 with trimethyl aluminum (TMA) and H_2O in a viscous-flow tubular reactor using in situ QCM measurements. We initially developed the ML code using simulated QCM data generated by a 1-D model of ALD transport and reaction. This allowed us to tailor the algorithm to ensure saturation of the TMA and H_2O ALD reactions and to converge efficiently on the optimal dose and purge times. We examined several ML algorithms including Bayesian optimization, physics-inspired optimization, and random optimization. An additional benefit of these simulations was that we could explore the effects of non-ideal behavior such as a CVD component to the surface reactions and strong interaction between the reaction products and the surface. Next, we interfaced the ML code to our ALD system and allowed the algorithm to optimize the TMA and H_2O timings. We observed rapid convergence, as predicted by our simulations, and found that the ML algorithm was capable of adapting to variations in the initial conditions such as the precursor partial pressures and the carrier gas flow rate. We are now building an array of QCM sensors to measure the thickness simultaneously at 10 locations along our flow tube, and we hope to report on ML opimization of thickness and uniformity using this array.

12:30pm **LI3-WeM-17 ALD/ALE Student Awards, Closing Remarks, & Sponsor Thank You**, *C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*;* ***Jean-François de Marneffe,*** IMEC, Belgium

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