Atomic Layer Etching
Room Plaza D - Session ALE+AF-MoA

Atomic Layer Etching Session V (1:30-3:30 pm)/ALD Fundamentals: Process Development (4:00-5:45 pm)

Moderator: Mike Cooke, Oxford Instruments Plasma Technology

1:30pm **ALE+AF-MoA-1 *In situ* Spectroscopic Methods for Atomic Layer Etching and Atomic Layer Deposition*, Yves Chabal*,** *J Klesko, A Dangerfield, J Veyan,* University of Texas at Dallas **INVITED**

As a relatively new technique, Atomic Layer Etching requires a fundamental understanding of the surface chemical processes that govern its operation. Most reported ALE processes are based on halogenation reactions followed by ion or noble gas atom bombardment, but there have recently been promising thermal ALE developments based on sequential fluorination and ligand exchange reactions. In all cases, knowledge of the fluorinated surface species and resulting surface composition after bombardment or exchange reactions is helpful to derive a mechanistic understanding of the surfaces. Such knowledge requires *in situ* characterization, in particular chemical bonding information that can be derived from vibrational spectroscopy.

We have developed reactors that can be used both for ALD and ALE, in which *in situ* IR spectroscopy is performed either in transmission for semiconductor substrates or reflection for metaling substrates, to examine gas phase or plasma-induced processes. We have also developed an ultra-high vacuum cluster tool in which IR spectroscopy, X-ray photoemission and Low Energy Ion Scattering can be performed on substrate subjected either to gas phase exposures or plasma treatment (remote plasma). Examples will be presented, taken mostly from ALD studies, which illustrate how mechanistic information can be derived from *in situ* IR spectroscopy, including the interaction of plasmas with oxides, nitrides and metal alloy films and the role of TMA in either stabilizing interfaces or enhancing surface reactions in ALD processes.

A schematic drawing of UHV cluster tool with in situ IR spectroscopy, XPS and LEIS is shown below.

2:00pm **ALE+AF-MoA-3 An *in situ* Optical Diagnostic Study of the Process Conditions that Affect the Etch per Cycle in ALE of SiO_2***, S Agarwal, **Ryan Gasvoda**, N Leick,* Colorado School of Mines*; A van de Steeg,* Eindhoven University of Technology, Netherlands*; R Ovanesyan, J Klein,* Colorado School of Mines*; R Bhowmick, E Hudson,* Lam Research Corp.

With the advent of 3-D architectures in semiconductor devices combined with shrinking device dimensions, precise patterning requirements pose new challenges for conventional plasma etching. One recently proposed technique to address the limitations of continuous plasma etching is atomic layer etching (ALE), which can simultaneously enable directional control, etch selectivity, and atomic-level removal rates. ALE has been extensively studied for a variety of materials including Al_2O_3, HfO_2, Si, and silicon-based dielectrics. In this study, we have explored the atomistic-level details of an ALE process for SiO_2 based on a CF_x deposition step using a C_4F_8/Ar plasma, which is followed by an ion-assisted Ar plasma activation step to release the fluorine in the CF_x film for SiO_2 etching.

Specifically, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE of SiO_2 to monitor the surface composition, and the net SiO_2 and CF_x film thickness, respectively. Infrared spectra recorded after the CF_x deposition half-cycle (spectrum in blue in Fig. 1) predominantly shows an increase in CF_x (x = 1, 2, 3) stretching vibrations at ~1230 cm^{-1}, but it also shows very weak C-O-Si and SiF_x (x = 1, 2, 3) stretching vibrations at ~1110 and ~970 – 1000 cm^{-1}, respectively. Given that the latter two vibrational bands appear as weak features, this indicate that a very thin mixing layer is formed at the SiO_2-CF_x interface compared to continuous etching of SiO_2.

After exposing the CF_x film on SiO_2 to an Ar plasma for 10 s, the spectrum in dark green in Fig. 1 clearly shows the simultaneous removal of SiO_2 and CF_x during Ar^+ activation. Further exposure to Ar plasma continues the etch of SiO_2 until the CF_x layer is completely removed as seen in the next four spectra. The last 10 s of Ar plasma exposure (red spectrum in Fig. 1) shows continued SiO_2 etching even after the removal of CF_x layer, which indicates that there is an additional source of etchant in the reactor. Sequential ALE cycles also show an increase in the etch per cycle as a function of cycle number (Fig. 2). This increase occurs even though the infrared spectra confirm that the deposition step remains reproducible from cycle to cycle as also seen in the inset in Fig. 2. Therefore, the increase in the etch per cycle occurs due to the Arplasma half-cycle as Ar^+ liberate CF_x radicals from the reactor walls that participate in the etching process. This chamber wall effect manifests as an increase in the etch per cycle since CF_x film accumulates on the chamber walls and, therefore, more F is available for etching in later cycles.

2:15pm **ALE+AF-MoA-4 New Innovative Etching Approaches for Future Generation by Controlling the Surface Reaction at Atomic-Level*, Masanobu Honda*,** *T Katsunuma,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

A new technology has been developed using the Atomic Layer Etching (ALE) and Atomic Layer Deposition (ALD) concepts. It has been applied to self-aligned contacts (SAC) and patterning processes, for the sub 7nm technology generation.

In the SAC process, ultra-high selectivity of SiO_2 etching towards SiN is required, for which we have developed Quasi-ALE technique for SiO_2 etching. We were able to significantly improve the trade-off between the etching ability of SiO_2 on the micro slit portions and SiN selectivity. Quasi-ALE precisely controls the reaction layer thickness of the surface, by controlling the radical flux and ion flux independently, and hence enables etching at lower ion energies.

On the other hand, in the patterning processes, the shrinking of critical dimensions (CD) without loading is mandatory. Therefore, we developed a new process flow that combines ALD technique and etching. With this method, we were able to achieve CD shrinking at atomic-layer level precision for various patterns, without causing CD loading. In addition, we were also able to uniformly control the CD shrinkage amount across the whole wafer. This is because this technique takes advantage of the deposition step which is independent of the pattern density and the location on the wafer by self-limited reactions.

As discussed earlier, the fine processing technology will become more important for future generation. In recent years, to meet the highly complex requirements imposed by device fabrication processes, alternative process was developed for thin layer etching [1]. We have made several improvements on this new approach and applied it to various etching processes [2]. In the presentation, the newly improved approach will also be introduced in addition to Quasi-ALE and CD shrinking technique without causing CD loading.

1. N Posseme, O Pollet and S Barnola 2014 Alternative process for thin layer etching: Application to nitride spacer etching stopping on silicon germanium Applied Physics Letters105 051605

2. Sonam D Sherpa and Alok Ranjan 2017 Quasi-atomic layer etching of silicon nitride J. Vac. Sci. Technol. A 35 01A102

2:45pm **ALE+AF-MoA-6 Controlled Layer-by-Layer Etching of ALD Grown Ta_2O_5 Thin Films*, Anil Mane*,** *J Elam,* Argonne National Laboratory

Precisely controlled layer-by-layer etching processes for metal oxide films are required to enable the fabrication of 3D-microelectronic devices such as semiconductor memories, logic, and MEMS. Ta_2O_5 is a high-k dielectric and is useful in flash memory as well as resistive random access memory (RRAM) devices. Here we developed a precisely controlled layer-by-layer etching process for Ta_2O_5 thin films using alternating exposures to MoF_6 and H_2O vapors. For example, etching of ALD Ta_2O_5 thin films deposited using either $TaCl_5$ or TaF_5 and H_2O can be perform in either a one-step, chemical vapor etching manner (CVEt) or in a layer-by-layer self-limiting controlled manner (ALEt). We used in-situ quartz crystal microbalance (QCM) measurements to monitor the deposition and etching of the Ta_2O_5 layers (Figure 1). Next, the etched Ta_2O_5 thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index. These ex-situ measurements confirmed the findings from our in-situ QCM studies. Here we will discuss the details of the self-limiting ALD growth and etching of Ta_2O_5 Thin films.

3:00pm **ALE+AF-MoA-7 Atomic Layer Etching Mechanism of 2D MoS_2 Layers*, Ki Seok Kim*,** *K Kim, Y Ji, G Yeom,* Sung Kyun Kwan University, Republic of Korea

The single MoS_2 monolayer has a $S_{(top)}$-Mo-$S_{(bottom)}$ crystal structure that is consisted of a three-atom-thick covalent bonds between Mo and S atoms; thereby, the ALE mechanism using Cl as the adsorption species and Ar^+-ion as the desorption species can be quite different from other two-dimensional (2-D) materials with one-atom-thick materials such as graphene. We have investigated that the MoS_2 ALE mechanism from bilayer MoS_2 to monolayer MoS_2 using controlled Cl radical adsorption and Ar^+-ion desorption as a function of Ar^+-ion desorption time with a monoenergetic Ar^+-ion energy of 20 eV. The result showed that Cl atoms

are adsorbed on top S atoms and trapped between top S atoms and Mo atoms by van der Waals force during the Cl radical adsorption. The reults also showed that the monolayer MoS_2 is sequentially removed from the top S atoms by S-Cl, Mo by Mo-Cl, and bottom S atoms by selective sputtering. XPS data showed no change of chemical composition and no structural damage on the exposed 2nd MoS_2 layer after one-cycle ALE. In addition, the MoS_2 FET fabricated with the monolayer MoS_2 obtained after the one-cycle MoS_2 ALE of a bilayer MoS_2 exhibited the similar electrical charteristics as those fabricated with a pristine monolayer MoS_2, therefore, nearly no electrical damage on the MoS_2 layer was ocurred by the MoS_2 ALE process. It is believed that the ALE technique used in the experiment can be applicable to all the layered TMD materials including MoS_2 for next generation nano-devices.

3:15pm **ALE+AF-MoA-8 ALD & Quasi-ALE Patterning Application in EUV Contact Etch***, **Hongyun Cottle**, D O'Meara, A Metz,* Tokyo Electron Limited*; P Biolsi,* TEL Technology Center, America, LLC*; S Nakamura, T Yang,* Tokyo Electron Limited*; M Honda,* Tokyo Electron Miyagi Ltd., Japan*; S Morikita,* Tokyo Electron Limited

Continued pitch scaling of semiconductor devices to 7nm node and beyond utilizing conventional 193i based multiple patterning techniques is rapidly driving up cost, complexity, and variability control. EUV patterning can be used to mitigate or delay the challenges of pitch scaling through multiple patterning, but introduces new challenges of its own. EUV lithography introduces new types of resists that are thinner and less etch resistant compared to conventional 193nm resists. Interactions of polymers with plasma etch environments can lead to large changes of the polymer material properties and the three-dimensional nanostructures they pattern. Mask deformation during such etch process can lead to changes in nanoscale topography of device features, often with undesirable consequences, such as increased LER and LWR, tip-to-tip degradation, and line wiggling. Plasma etch faces a significant challenge to optimize its process window to enable high yields with EUV patterning.

This paper presents the synergetic combination of ALD & Q-ALE in EUV contact mask etch to overcome the above-mentioned EUV lithography changelings. ALD application at mask open level improves incoming LWR/LER and defines what can be transferred to final etch product. Q-ALE mask open improves EUV photoresist etch selectivity by greater than three-fold while maintaining critical feature dimensions, such as elliptical contact minor vs major axis CD ratio. By utilizing a direct current superposition (DCS) technology, EUV photoresist can also be treated to improve not only its etch resistant, but also LER and LWR. These unique processes (ALD vs. Q-ALE vs. DCS) can be applied independently or in combination utilizing Tokyo Electron advanced etchers. Through their accumulative effects, these processes offer a wide range of etch capabilities to enable EUV lithography to 7nm and beyond.

Reported is the structural characterization pre and post-etch detailing LER and LWR improvement, and shrink ratio control. In addition, a mechanistic model will be proposed based on thin film compositional analysis and process trend data.

4:00pm **ALE+AF-MoA-11 Boron Nitride Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)***, **Jaclyn Sprenger**, H Sun, A Cavanagh, S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. This temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine ($B_3N_3H_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~0.45 Å/cycle for electron energies of 100 eV with an electron current of 100 µA for 60 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 90 nm was deposited after 2000 EE-ALD cycles (see supplemental Figure 1).

Film composition was studied with *ex situ* XPS (see supplemental Figure 2). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm^{-1} that is consistent with hexagonal BN.

Doubling the electron emission current used for BN film growth from 100 µA to 200 µA with exposure times of 60 s yielded slightly lower film growth rates. However, these films had a higher measured index of refraction. This suggests that an electron current of 100 µA may be sufficient to remove all the surface hydrogen in the electron beam. The fairly flat BN thickness spatial profiles are also consistent with self-limiting hydrogen desorption. The higher electron current of 200 µA for 60 s does appear to increase the film density.

[1] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, "Electron Enhanced Growth of Crystalline Gallium Nitride Thin Films at Room Temperature and 100°C Using Sequential Surface Reactions", *Chem. Mater.* **28**, 5282 (2016).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun and S.M. George, "Electron Enhanced Atomic Layer Deposition (EE-ALD) of Silicon Films at Room Temperature", Presentation at ALD2016 in Dublin, Ireland.

4:15pm **ALE+AF-MoA-12 Catalyzed Atomic Layer Deposition of Silicon Oxide at Ultra-low Temperature using Alkylamines***, **Tirta Rona Mayangsari**, J Park, L Yusup, J Gu,* Sejong University, Republic of Korea*; J Yoo, H Kim,* JUSUNG Engineering, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The dielectric spacer in multipatterning process such as self-aligned double patterning (SADP) or self-aligned quadruple patterning (SAQP) has been adopted to increase the density of line pattern with only single exposure. Deposition of the dielectric spacer directly on the photoresist patterns instead of the hardmask patterns would reduce several process steps. For this purpose, ultra-low temperature deposition of the spacer film is highly required to avoid the distortion of the underlaying photoresist patterns. Atomic layer deposition (ALD) processes of SiO_2 dielectric thin film at ultra-low temperature have been studied by using pyridine catalyst [1] or O_2 plasma [2]. Catalyzed ALD of SiO_2 is especially suitable for the cost-effective SADP or SAQP process flow, because it can avoid the damages of the underlying photoresist patterns by O_2 plasma. However, in the catalyzed ALD process using pyridine, the generation of salts is still an issue as a result of reaction between the catalyst and ALD reaction byproducts, HCl [3]. To resolve this issue, catalyst having less reactivity with HCl is needed. In the present study, we simulated the reaction of various catalysts with HCl as well as the interaction between catalysts and precursors by density functional theory (DFT) calculation.

Lewis-base amine catalysts with different alkyl ligand and hydrogen concentration were studied, and silicon chlorides with different numbers of silicon and chlorine atoms were investigated. The length and the energy of hydrogen bond between catalyst and water molecule were calculated for each catalysts to expect the catalytic activity, and the energies of the formation and desorption of the catalyst-HCl salt were also calculated. The effects of molecular structures of catalysts and silicon precursors on the catalytic activity and the salt formation were confirmed by in-situ FTIR analysis. Finally, the growth rate, the chemical composition, and the step coverage of the deposited films were analyzed for different combinations of catalyst and silicon precursor.

[1] J.W. Klaus et al, Science, 287 (1997) 1934.

[2] G. Dingemans et al, ECS Transactions, 35 (2011) 191.

[3] Y. Du et al, J. Phys. Chem. C, 111 (2007) 219.

4:30pm **ALE+AF-MoA-13 Low Resistance ALD TiN from Low Temperature Thermal N_2H_4 + $TiCl_4$***, **Steven Wolf**, M Kavrik, J Park,* University of California San Diego*; R Holmes, D Alvarez, J Spiegelman,* RASIRC*; A Kummel,* University of California San Diego

Titanium nitride (TiN) has been extensively studied in semiconductor devices because of its ideal thermal, mechanical, and electrical properties and its ability to act as a metal diffusion barrier [1]. ALD TiN has previously been performed using a wide range of Ti precursors including halides (i.e. TiI_4, $TiCl_4$) and metal organics (i.e. TDMAT, TEMAT), as well as nitrogen sources (thermal/plasma NH_3, N_2/H_2, etc). Metal halide precursors are preferred over metal organic grown films that typically contain high levels of carbon and oxygen contamination; this contamination has been correlated with an increase in TiN film resistivity [2]. Plasma enhanced-ALD TiN has been shown to achieve optimal growth rates with lower contamination at temperatures below 350°C, but the film and underlying substrate can suffer from plasma induced damaged [1,3]. In this study, low temperature thermal ALD TiN from anhydrous N_2H_4 and $TiCl_4$ was

performed on a SiO_xN_y substrate, and the deposited films were studied using x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). In addition, the resistivity of thin TiN films was measured using a modified four-point probe measurement, in which 30nm thick Ni dots with 150µm diameter and 250µm spacing were deposited on top of ALD TiN films.

SiO_xN_y substrates underwent an ex-situ degrease procedure with acetone, methanol and water before being loaded into vacuum. A 275°C UHV anneal was performed to remove surface hydrocarbon. Subsequent cycles of TiN ALD at temperatures between 275°C and 350°C were performed resulting in an estimated 3nm thick film with a Ti/N ratio of ~3/4 with chlorine comprising ~10% in the normalized XPS spectrum. Uniform deposition with subnanometer RMS roughness was seen from STM and AFM measurements. After depositing Ni dots and performing a modified four-point probe measurement, film resistivity was estimated at ~176 µΩ-cm. In conclusion, the thermal low-temperature TiN ALD using anhydrous N_2H_4 and $TiCl_4$ was performed and the subsequent low impurity TiN film's chemical, topographical and electrical properties were characterized.

[1] Elers, K-E., et al. "Diffusion barrier deposition on a copper surface by atomic layer deposition." *Chemical Vapor Deposition* 8.4 (2002): 149-153.

[2] Musschoot, Jan, et al. "Atomic layer deposition of titanium nitride from TDMAT precursor." *Microelectronic Engineering* 86.1 (2009): 72-77.

[3] Suehle, J. S., et al. "Challenges of high-k gate dielectrics for future MOS devices." *Plasma-and Process-Induced Damage, 2001 6th International Symposium on*. IEEE, 2001.

4:45pm **ALE+AF-MoA-14 Study of the Isotropic Behavior of AZO Conductivity Deposited by Atomic Layer Deposition - Effect of Film Thickness***, **Benoit Dugrenil,*** Microoled - CEA Leti, France*; S Guillamet, M Thomschke,* Microoled Company*; M Tournaire, B Aventurier, L Mollard, T Maindron,* CEA-Leti, France

Keywords: ALD, TCO, transparent electrode, OLED, anisotropic conductivity

Al-doped ZnO (AZO) is one of the most recently studied Transparent Conductive Oxides (TCO), especially because of its numerous attractive properties as electrode in OLED, OPV or OTFT. Atomic Layer Deposition (ALD) allows a precise control of AZO performances versus deposition temperature, doping ratio and thickness. Conventional AZO measurements using four-point probe setup or Hall effect (fig 1 a) are mainly representative of the combination of vertical and lateral conductivity of the film. However, when those TCO have to be integrated into an OLED stack as transparent electrode, carrier injection is made in the vertical direction (fig 1 b). We believed that AZO is an anisotropic material, particularly because of its growth as nanolaminate, i.e. alternating ZnO bulk layers with Al_xO_y interlayers in ALD mode.

In this work, we want to study the anisotropy of the electrical conductivity of AZO films, as depicted in figure 1 a and 1 b. Furthermore, as the AZO film thickness impacts the electro-optical characteristics, its influence on the vertical conductivity needs to be highlighted.

We firstly investigated the major differences between very thin films (approximately 10 nm), and thicker AZO (60 nm, 110 nm) deposited on 200 mm silicon and silicon oxide wafers, respecting exactly the same growth conditions. The resistivity decreases from ~ 100 mΩ.cm for very thin films to 3 mΩ.cm when the thickness is increased above a hundred of nanometers. Identical variations have been measured for the square resistance and are consistent with other studies [1]. These trends are known and can be attributed to the growth parameters like preferential orientation, nucleation delay and ionized impurities scattering [2, 3].

In a second step, the same AZO recipes were deposited onto structured TiN layers, where the TCO films can be evaluated in the OLED configuration, as an anode (fig 1 b). In order to correlate the AZO behavior in both configurations and function of the deposited thicknesses, attention will be carried out on crystalline profile using XRD measurements and onto electro-optical characteristics of the OLED.

[1] Pollock, E. B *et al*. Journal of Vacuum Science & Technology A 32, 041516 (2014). doi: 10.1116/1.4885063

[2] Luka, G.*et al*. Journal of Materials, 1810-1815 (2011). doi: 10.1007/s10854-011-0367-0

[3] Mundle, R., Pradhan, A. K. Journal of Applied Physics, 115, 183503 (2014).doi:10.1063/1.4875536.

5:00pm **ALE+AF-MoA-15 Growth Behaviour and Stability of Atomic Layer Deposited MoO_3 by $Mo(CO)_6$ and H_2O/O_3 Precursors***, **Perttu Sippola,*** Aalto University, Finland*; Z Zhu,* Beneq Oy*; T Sajavaara,* University of Jyväskylä, Finland*; H Lipsanen,* Aalto University, Finland

Molybdenum trioxide has been shown to be a lucrative material e.g., for catalysis [1] and electrochromic applications [2]. This applicability can be credited to the multitude of oxidation states and polymorphs of the compound. Despite MoO_3 complex chemistry, ALD presents a promising and efficient way of growing amorphous MoO_3 thin films. Still, mainly the *in-situ* growth and annealing behavior has been studied. [3] Therefore, we present a growth, structure and chemical analysis of as-deposited MoO_3 ALD thin films.

MoO_3 thin films were deposited on silicon with Beneq TFS-500 using $Mo(CO)_6$ and H_2O/O_3. The effect of precursor doses to the growth behavior and physical properties was studied immediately after the ALD with ellipsometry and later with XRR. Moreover, chemical and elemental analysis with ATR-FTIR and ToF-ERDA, respectively, were performed.

With ellipsometry, the ALD-window of the process was determined to be approximately in the range of 165-175 °C. Thus, deposition temperature of 170 °C was selected. The pulse time saturation of 55 °C heated $Mo(CO)_6$ was studied to take place around 2 s. The overlapping H_2O/O_3 pulsing time ratio in seconds was varied from 0/2-3/2. The O_3-only precursor yielded GPC of 0.65 Å/cycle and for the H_2O added pulses GPC was 0.75 Å/cycle. The ATR-FTIR spectra showed that unlike the other samples, the 2/2 mixture did not had an emphasized band at ~3650 cm^{-1} which is usually attributed to the presence of –OH groups.

The further studies suggest that prolonged storage of the samples in ambient conditions produced structurally differing surface layer on top of the original MoO_3 thin films. The XRR analysis showed a surface layer of 6 nm with a density of 2.8 g/cm^3 on average while the underneath MoO_3 layer showed density of 4.3 g/cm^3. Also, the refractive index value reduced on average from 2.03 to 1.90 between the fresh and aged samples. Moreover, the ToF-ERDA elemental depth profile results revealed that the C (2.5 at.%), H (14 at.%) and N (3.1 at.%) impurities are concentrated to the surface in the thin films. Still, the average O/Mo ratio was 3.1, being very close to stoichiometric.

Due to the presence of the parasitic surface layer, valid differences on the structural and elemental constitution of the different samples could not be identified. Therefore, this research concludes that the $Mo(CO)_6$ and H_2O/O_3 ALD thin films are not chemically stable in ambient conditions without further in-line-processing such as surface passivation.

[1] K. V.R. Chary, et al., J. Catal. (2004) 226, 2

[2] T. Ivanova, et al., Mat. Sci. Eng B Solid (2005) 119, 3

[3] M. Diskus, et al., J. Mater. Chem. (2011) 21, 3

5:15pm **ALE+AF-MoA-16 Characterization of Al_2O_3 and HfO_2 Grown on Metal Surfaces with Thermal and Plasma Enhanced Atomic Layer Deposition***, **Haiping Zhou,*** *Y Fu, M Mirza,* University of Glasgow, UK

Atomic layer deposition (ALD) is potentially a very suitable deposition technology to grow ultra thin films with excellent thickness control, good conformity on high aspect ratio structures, and less defects. Al_2O_3 and HfO_2 are well-established high-k materials to replace SiO_2 in transistor and capacitor applications. To grow high quality ALD films with low leakage current, high breakdown electric field and dielectric constant, it is important to understand the impact of both plasma enhanced ALD (PEALD) with O_2-plasma and thermal ALD with H_2O on the interface between ALD film and substrate surface, and also the impact of the interface on the quality of ALD films.

We present the electrical and chemical characterizations of Al_2O_3 and HfO_2 films directly grown on Au, Ti and TiN surfaces. Metal Insulator Metal (MIM) capacitors with 10nm of Al_2O_3 or 10nm of HfO_2 as a dielectric layer were realized. Our results show that (1) the Al_2O_3 film grown by TMA metallic precursor and O_2-plasma has the highest breakdown electric field of 6.74 MV/cm, and the lowest leakage current of 8.6e-8 A/cm^2 at 2 MV/cm, which indicate that this 10nm of Al_2O_3 layer is high quality dielectric film with low pin-hole density and defects; (2) the HfO_2 film grown by TEMAH metallic precursor and H_2O has the lowest breakdown electric field of 3.95 MV/cm, and the highest leakage current of 7.6e-7 A/cm^2 at 2 MV/cm, which indicate that this 10nm of HfO_2 film has more pin-holes and defects; (3) the Al_2O_3 film grown by TMA and H_2O, and the HfO_2 film grown by TEMAH and O_2-plasma have the breakdown electric fields of 6.56 and 4.28 MV/cm, and the leakage currents of 2.40e-7 and 2.33e-7 A/cm^2 at 2 MV/cm, respectively; (4) both the Al_2O_3 and HfO_2 films

grown by the PEALD with O_2-plasma show better qualities than that grown by the thermal ALD with H_2O; (5) the Al_2O_3 and HfO_2 with O_2-plasma processes do not show plasma-induced damage based on the tests of Van der Pauw (VdP) samples made from InGaAs-InAlAs layer structure with channels buried ~ 30 nm from the surface.

To further investigate, understand and optimize the ALD processes, Auger energy spectroscopy (AES) and high-resolution scanning Auger microscope (SAM) are used to analyze the chemical compositions and distributions in the interface between the ALD films (Al_2O_3 and HfO_2 grown with O_2-plasma and H_2O) and the metal surfaces (Au, Ti and TiN) without exposing the ALD films to air.

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Sippola, P: ALE+AF-MoA-15, **3**
Spiegelman, J: ALE+AF-MoA-13, 2
Sprenger, J: ALE+AF-MoA-11, **2**
Sun, H: ALE+AF-MoA-11, 2
— T —
Thomschke, M: ALE+AF-MoA-14, 3
Tournaire, M: ALE+AF-MoA-14, 3
— V —
van de Steeg, A: ALE+AF-MoA-3, 1
Veyan, J: ALE+AF-MoA-1, 1
— W —
Wolf, S: ALE+AF-MoA-13, **2**
— Y —
Yang, T: ALE+AF-MoA-8, 2
Yeom, G: ALE+AF-MoA-7, 1
Yoo, J: ALE+AF-MoA-12, 2
Yusup, L: ALE+AF-MoA-12, 2
— Z —
Zhou, H: ALE+AF-MoA-16, **3**
Zhu, Z: ALE+AF-MoA-15, 3