ALD Applications
Room Van Rysselberghe - Session AA2-TuA

ALD for BEOL

Moderators: Scott Clendenning, Intel Corporation, John Conley, Oregon State University

4:00pm **AA2-TuA-11 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Titanium Nitride Using Ammonia Reactive Background Gas***, **Zachary Sobell**, S. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiN_x films. In addition, a new method of EE-ALD was employed with a reactive background gas (RBG) concurrently present during the EE-ALD process (shown in Figure 1). Using the RBG is possible because the hollow cathode plasma electron source (HC-PES) employed for this EE-ALD can operate with reactor pressures in the mTorr range. EE-ALD with a RBG displayed rapid film nucleation and produced continuous, low resistivity ultrathin films. The use of the RBG opens many potential routes for novel EE-ALD film deposition. For example, these ultrathin EE-ALD films should be useful for barriers in backend interconnects.

The TiN_x EE-ALD was performed using tetrakis(dimethylamido) titanium (TDMAT) as the Ti precursor. The EE-ALD was performed using sequential exposures of TDMAT and electrons. During these sequential exposures, ammonia (NH_3) was present continuously in the reactor as the RBG at ~1 mTorr. NH_3 is believed to interact with the electron beam and liberate H and N radicals. The N radicals may facilitate Ti nitridation and the H radicals may remove C as CH_4. Using a RBG was not possible during earlier EE-ALD work with an electron gun because the electron gun has a hot filament that would react with the RBG.

The TiN_x EE-ALD films were grown with the RBG at low temperatures of T<70 °C. In situ ellipsometry demonstrated that the TiN_x EE-ALD films nucleated rapidly on both Si native oxide films (shown in Figure 2) and Si_3N_4 films. The TiN_x EE-ALD films produced using the NH_3 RBG also displayed excellent properties. The composition of the TiN_x EE-ALD films using the NH_3 RBG was close to 1:1 Ti:N as measured by XPS. The carbon content in the TiN_x EE-ALD films was ~2 at.% by ex situ XPS. In contrast, the carbon content was ~60 at.% without the NH_3 RBG. The as-deposited TiN_x EE-ALD films also displayed ultralow resistivities. In situ ellipsometry measured resistivities as low as 105 μΩ-cm (shown in Figure 2). Ex situ spectroscopic ellipsometry obtained resistivities as low as 115 μΩ-cm using a model that agrees well with literature values for the optical properties of TiN. Ex situ four-point probe also measured resistivities as low as 123 μΩ-cm. The TiN_x EE-ALD films were crystalline as determined by GI-XRD. XRR modeling also revealed that the films were dense at approximately 98% of the theoretical bulk density of 5.24 g/cm^3 for TiN.

4:15pm **AA2-TuA-12 Atomic Layer Deposition of MoNx Thin Film Using New Synthesized Liquid Mo Precursor***, **Byunguk Kim**, T. Kang, S. Kim, H. Jeon,* Hanyang University, Korea

Recently, as the resistivity of the metal thin film is increased due to the scaling down of the memory device,interest in Mo metal, which is a metal with low resistivity, is increasing. However, nucleation delay occurs during the deposition process due to the nature of the metal film such as Mo film.To prevent this, the need for a low-resistivity seed layer is emerging. Among them, MoNx film is spotlighted as a seed layer. Because MoNx thin film has excellent thermal stability, low resistivity, and excellent process efficiency because it uses the same precursor as Mo film.

3D-NAND, which is spotlighted as a next-generation memory device, is a high aspect-ratio device, and since a thin film must be deposited with high uniformity on the upper and lower layers, the need for the ALD process is emerging. This is because the ALD process is easy to control thickness and has excellent step characteristics. Therefore, an experiment was performed to deposit a low-resistivity MoNx film using the ALD process. Also, recently, a halide solid precursor such as MoO2Cl2 is used to deposit Mo/MoNx film. However, in the case of a solid precursor, it is difficult to maintain process conditions. Therefore, in this study, a self-synthesized liquid Mo precursor was used to deposit the MoNx film. As reactants, NH3 gas and H2 gas were used. The reason that H2 gas as well as NH3 gas is used as a reactant is that a MoNx film with less impurities can be deposited by reacting with NH3 gas after removing the ligand using H2 gas. XRR, AES, XRD and 4-point probe were used to evaluate the physical and electrical properties of the deposited MoNx film.

As a result of AES analysis of the MoNx film deposited using the ALD process, Mo and N were 62-64% and 29-32%, respectively, and the impurity, C, was detected to be less than 2% and O was detected to be about 5-6%. Additionally, the sheet resistance of the deposited MoNx film was confirmed to be 400ohm/□ confirming that it was a low-resistivity film.

Through the results of this study, it is possible to establish the MoNx film deposition process, which is considered as a next-generation metal seed layer, and we think that the results of this study will be widely used in the next-generation memory device industry.

4:30pm **AA2-TuA-13 Atomic Layer Deposition of Tungsten Nitride Thin Film using WCl_5 as a Fluorine-free W Precursor and its Application into the Diffusion Barrier for Cu and Ru Interconnects***, **Kang-Min Seo**, G. Bea, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Tungsten(W) is applied to the current semiconductor devices such as W-plug process, metal gate of 3D NAND flash, or bit line of DRAM, due to its extremely low bulk resistivity. Additionally, some thin films of other tungsten compounds like WN_x, WC_x, and WN_xC_y also have an important role in the current semiconductor devices applications as a diffusion barrier. On the other hand, as the size of semiconductor devices has become extremely narrow (in few nm), it has become difficult to deposit a thin film with a precise thickness in a complex structure. In this regard, atomic layer deposition (ALD) seems to be the best option to prepare any thin film which would find its suitability in future technology. So far, the ALD of W or W-based thin films are deposited using WF_6 as a precursor. However, due to the highly corrosive and toxic properties of the F and by-products such as HF, WF_6 thin film process has obvious limitations. In this study, ALD processes using tungsten pentachloride (WCl_5) as an F-free W precursor and various reactants such as NH_3, TBH (tert-butyl hydrazine) molecules, and its plasma as reactants were reported. Preliminary results indicated that, among these reactants, the best quality ALD-WN_x film can be obtained using N_2 + H_2 mixture plasma as a reactant, and further experiments were done mainly using N_2 + H_2 mixture plasma. The deposition was done with a temperature ranging from 200 to 300 ℃at the chamber pressure of ~ 1 Torr. Self-limited growth behavior, the key characteristic of the ALD process was first investigated at the deposition temperature of 250 ℃.At the optimized pulsing condition, the saturated growth per cycle (GPC) was ~1.1 Å. The properties of ALD-WN_x with deposition conditions were analyzed using various tools such as XRD, XPS, 4-point probe, SEM, SIMS, RBS, TOF-ERD, and TEM. The XRD analysis showed that the WN_x thin films have a mix-phase of WN and W_2N. And XRD on WN_x films annealing at high temperature showed a high thermal stability and phase transition (WN to W_2N) at high temperature. Furthermore, the RBS and TOF-ERD analysis showed that the composition of which WN_x thin films has a phase of WN rather than W_2N and reveals relatively low impurities(oxygen, chlorine). Finally, we applied the deposited ALD-WN_x as a diffusion barrier/glue layer for Cu and Ru metallization and the results will be reported in the conference.

4:45pm **AA2-TuA-14 Thermal Atomic Layer Deposition of Ru With H_2 Molecules for Emerging Ru Interconnects***, **Yohei Kotsugi**,* Chemical Materials Development Department, TANAKA Precious Metals, Japan*; Y. Kim, T. Cheon, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Ru has been in the limelight as one of the alternatives for Cu interconnects due to its shorter electron mean free path than that of Cu. Therefore, in this regard, a lot of Ru-ALD processes have been investigated. However, most of them has been deposited with O_2 as a reactant gas, and there is an inevitable concern that the oxidation of the metallic underlayer may occur even if the Ru film itself is not oxidized. For these reasons, plasma-enhanced ALD technologies have often been proposed, but they also have a problem of the limited conformality on a high AR 3D structure. Here, we introduce plasma-free atomic layered deposition of Ru using H_2 molecule as a non-oxidative reactant and a Ru metal-organic precursor. The film properties, such as the crystallinity, resistivity, impurities contents, and grain size, were compared with those of the film deposited using the same Ru precursor and O_2. The deposition conditions were optimized with regard to the already reported O_2 process. A thin Ru film of ~4 nm was deposited with∼100% step coverage on a narrow dual-trench substrate. The low film resistivity of as grown film of ∼23.0 μΩ·cm was further reduced to low resistivity of ∼10.7 μΩ·cm by the post-annealing (700 °C) treatment. These results suggested that H_2–based thermal ALD process without using plasma-enhanced techniques can also produce high-quality Ru films.

However, the resistivity and impurity concentration were slightly higher than those of the O_2 process. Moreover, this H_2-based ALD process has the disadvantage that it takes longer time to complete one cycle than the O_2-based one. In order to overcome the above issues, we designed a new method to minimize the oxidation of under substrates, whereas the film quality was as high as or better than that of the films deposited using O_2 as a reactant. The low resistivity comparable to that of the O_2-based process was obtained in the 40 nm-thick ALD Ru films and it should be noted that, for ultrathin films of 10 nm or less, its resistivity value was even lower than that of O_2–based one. Additionally, the formation of highly pure Ru film with negligible carbon and oxygen impurities were confirmed by secondary ion mass spectroscopy and excellent step coverage on a narrow dual-trench substrate was demonstrated using transmission electron microscopy analysis. The obtained high-quality Ru film can have the potential to be adopted as a Cu substitute material.

5:00pm **AA2-TuA-15 The Oxygen-Free Thermal ALD and Area Selective ALD of Ruthenium Film***, I. Liu,* SAFC HITECH TAIWAN CO., LTD., Taiwan*;* ***Bhushan Zope****, G. Liu,* EMD Performance Materials Corp.*; J. Woodruff,* EMD Electronics*; J. Chiu,* SAFC HITECH TAIWAN CO., LTD., Taiwan

Ru thin films have been extensively studied for various applications in semiconductor devices such as electrodes for DRAM and MOSFET due to the good stability, low resistivity (7.1 μΩ·cm in the bulk), and high work function (4.7eV). Conventional methods to prepare Ru film are to use plasma-enhanced atomic layer deposition (PEALD) and thermal ALD with oxygen coreactant. As technology nodes continue to shrink, the plasma process may cause poor uniformity and conformality of deposited Ru film. Oxygen coreactant may also result in the oxidation of Ru film or underlying materials. Therefore, oxygen-free thermal Ru processes attract the attention of semiconductor industry to fabricate future devices.

In this study, the newly developed oxygen-free thermal Ru ALD process is reported. Highly uniform, smooth and conformal Ru films were deposited by thermal atomic layer deposition from Ru precursor, RuEM8, and H2 at low deposition temperature (235 ~ 275 ℃). The GPC of RuEM8/H2 process is 0.6Å/cycle. The Ru films grown on SiO2 were smooth (Rq = ~0.22nm) with low resistivity (20 uohm-cm for 8nm film), which indicates good continuity. XPS analysis shows that the Ru films are pure, and the concentration of impurity is under the detection limit. Conformality of Ru growth were studied on via with aspect ratio 20:1. The preliminary results suggest that the conformality can be optimized to 85 ~ 90% (Figure 1).

In addition to basic Ru film growth, area selective ALD (ASALD) applications of RuEM8/H2 process were also studied. For patterning of microelectronics, metal on metal ASALD is becoming an important need to grow metal capping layer or seed layer for gapfill. By incorporating the inhibitor in the process, the RuEM8/H2 can selectively grow Ru film on Ru surface, but not on SiO2 surface. The selectivity of 7.6 (thickness of Ru on Ru / thickness of Ru on SiO2) for RuEM8/H2 ASALD process was achieved (Figure 2)

5:15pm **AA2-TuA-16 ALD-Prepared 2D Transition Metal Dichalcogenides as Diffusion Barriers in Interconnects***,* ***Sanne Deijkers****, A. de Jong,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM Belgium*; E. Kessels, A. Bol, A. Mackus,* Eindhoven University of Technology, The Netherlands

For sub-5 nm technology nodes scaling of interconnects is becoming a real challenge. This holds particularly for Cu diffusion barriers, as the typically used TaN/Ta layers fail at thicknesses below 3 nm [1]. The impossibility to scale the diffusion barrier limits the dimensions of the Cu in the interconnect and thus increases the resistivity drastically. To reduce the thickness of the barrier, the TaN/Ta layers could be replaced by atomically-thin 2D transition metal dichalcogenides (TMDs). In this work we report on the diffusion barrier performance of 2D-TMDs prepared by atomic layer deposition (ALD). Up to this point, literature reports concerning 2D-TMDs as barrier layers are limited to chemical vapor deposition (CVD) processes [2]. The advantages of using ALD are the BEOL-compatible temperatures, the excellent control of both film thickness and morphology, and the high conformality that can be obtained for continuous ultra-thin films on demanding nanostructures.

Various 2D-TMDs have been deposited by ALD at BEOL-compatible temperatures on 90 nm thermal SiO_2. MoS_2 has been deposited using $Mo(NMe_2)_2(N^tBu)_2$ as precursor and H_2S containing plasma as co-reactant [3]. Variations in the process conditions, such as the deposition temperature and the implementation of additional plasma steps, result in different morphologies including amorphous, crystalline and out-of-plane-oriented (OoPO) nanolayers [3]. The barrier performance of the barrier layers against Cu diffusion has been characterized by time-dependent dielectric breakdown (TDDB) tests. Additional insight into the Cu diffusion mechanism through the barrier layer has been obtained from scanning electron microscopy inspection. The results show that polycrystalline MoS_2 displays good barrier performance with a median time-to-failure ($TTF_{50\%}$) of $(8 \pm 1)\cdot 10^3$ s at an electric field of 6 MV/cm. This is a substantial improvement compared to barrierless samples, where $TTF_{50\%} = (1.9 \pm 0.3)\cdot 10^2$ s.

[1] Lo *et al., npj 2D Mater Appl* **1**, 42, (2017)

[2] Lo *et al., J.Appl.Phys.* **128**, (2020)

[3] Sharma *et al.,Nanoscale*, **10**, 8615, (2018)

5:30pm **AA2-TuA-17 Evolution of Structural and Electrical Properties of Molecular Layer Deposited Hafnicone Films after Thermal Processing for Applications in Low-*K* Etch Stops***,* ***Vamseedhara Vemuri,*** Lehigh University*; S. King,* Intel, USA*; N. Strandwitz,* Lehigh University

Molecular layer deposition (MLD) yields in conformal hybrid organic-inorganic thin films with precise control over the thickness and conformality similar to atomic layer deposition (ALD). The MLD films have in-organic constituents bonded to organic moieties. This work examines the effect of temperature on the electrical, chemical and structural properties of as-deposited MLD thin films.

The hafnicone films were grown using tetrakis(dimethylamido)hafnium (TDMAH), and ethylene glycol (EG) at 120 ºC. The as-deposited hafnicone films were annealed from 150-350 ºC in an inert atmosphere under a vacuum.

The incorporation of organics and the difference in the chemistry of hafnicone from hafnia films is observed using the ex-situ fourier transform infrared spectroscopy (FTIR). Hafnicone films show a decrease in the intensity of hydrocarbon peaks, whereas the intensity of hydroxyl peaks decreases with annealing in the case of hafnia films. The crystallization behaviour of the hafnia and hafnicone films is probed using the in-situ x-ray diffraction. The ethylene glycol moieties present inside the hafnicone delay the crystallization during annealing when compared to hafnia films. The removal of organics in the hafnicone films may be causing structural collapse and decrease in thickness leading to densification which can be observed by ex-situ X-ray reflectivity data. The dielectric constant of the as-deposited and annealed hafnicone films is lower than as-deposited and annealed hafnia. The dielectric constant of the hafnicone films increases with annealing and can be attributed to removal of organics and densification as observed by FTIR and x-ray reflectivity whereas the dielectric constant of the hafnia films decreases with annealing. This decrease can be attributed to the removal of hydroxyl species after annealing as observed by FTIR. The etch rate of as-deposited hafnicone films is measured in CF_4/O_2 plasma which decreases with increasing annealing temperature to 350 ºC, whereas the etch rate of the hafnia films stays constant even after annealing.

The dielectric constant of hafnicone is much lower than hafnia, and the etch rate of the 350 ºC annealed hafnicone film is similar to the etch rate of hafnia. Our study thus proves that the MLD films offer a high degree of tunability and can be used as potential low-*k* etch stops.

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