ALD Applications
Room On Demand - Session AA8
Memory Applications: DRAM

AA8-1 Influences of Oxygen Source and Substrate Temperature on Growth Mechanism of Atomic Layer Deposited Magnesium Oxide Using Bis(Cyclopentadienyl)Magnesium Precursor*, **Bowen Wang**, J. Choi, H. Kim, S. Hyun, H. Lee, C. Hwang,* Seoul National University, Korea (Republic of)

This research mainly studied the dissimilarities of MgO thin film's growth mechanisms in the atomic layer deposition (ALD) process depending on the oxygen sources, such as O_2 plasma, O_3, and H_2O (Fig. 1a, b). The bis(cyclopentadienyl)magnesium (Cp_2Mg) was adopted as the Mg-precursor. The effects of the oxidizing power and the temperature from 230℃ to 390℃ on the Cp-ring rupture reactions in the ALD process were analyzed by ex-situ techniques, such as X-ray diffraction/reflectometry, X-ray photoelectron spectroscopy (Fig. 1c and d), time of flight secondary ion mass spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy and transmission electron microscopy (Fig. 2a, b). It was intended to examine the crystallization, impurities and their depth profiles, stoichiometric ratio, surface/interface bonding, relative volumetric density. At relatively low substrate temperature (~ 250℃), albeit the similar crystallization and surface morphology were measured by glanced incidence X-ray diffraction and the field emission scanning electron microscope, O_2 plasma-enhanced ALD MgO showed the least impurity level and highest density. At the same time, the O_3-based thermal ALD-MgO exhibited the lowest density and highest impurity level among those three co-reactants. Unlike the overgrowth and void formation (Fig. 2b) at the growth temperature of 290℃, the O_3 ALD showed a comparably lower impurity level than the plasma-enhanced ALD at 335℃. Figure 1e shows the suggested ALD reaction mechanism. This was corroborated by the electrical characteristics using the planar metal-insulator-metal capacitors (metal layer was TiN). Furthermore, the pre-, post-annealing conditions were optimized for the optimal leakage current and dielectric constant of ALD-MgO.

AA8-2 Atomic Layer Deposition of Y-Doped TiO_2 Thin Films to Decrease the Leakage Current for DRAM Capacitor Applications*, **Tae Kyun Kim**, C. Hwang,* Seoul National University, South Korea

This work reports the electrical behavior of Y-doped TiO_2 (YTO) thin film as a dielectric layer for a capacitor of dynamic random access memory. The electrical performance of YTO thin films is comparable to that of Al-doped TiO_2 (ATO) thin films (Fig. 1(a)), which is well-known for its excellent leakage current property among other series of doped rutile TiO_2 thin films [1]. Nonetheless, YTO thin films appear to suppress the leakage current via a different mechanism from that of the ATO thin films. The large ionic size of Y ion compared with the Ti inhibits the efficient diffusion of them into the lattice of the rutile TiO_2 thin film, which results in a nano-laminate structure (Fig. 1b). In contrast, the small ionic size of Al in ATO fluently diffused into the TiO_2 film and form acceptor states. Therefore, it could be guessed that the leakage current suppression mechanism in YTO film is similar to that in the $ZrO_2/Al_2O_3/ZrO_2$ case, where the interrupted columnar grain structure of the ZrO_2 layer has contributed to the leakage current control.

AA8-3 Improved Properties of the Atomic Layer Deposited Ru Electrode for Dynamic Random-Access Memory Capacitor Using Discrete Feeding Method*, **Dae Seon Kwon**,* Seoul National University, Korea*; W. Jeon,* Kyung Hee University, Korea*; D. Kim, T. Kim, H. Seo, J. Lim, C. Hwang,* Seoul National University, Korea

A ruthenium (Ru) thin film as a bottom electrode of dynamic random-access memory (DRAM) capacitor was grown via atomic layer deposition (ALD) with a discrete feeding method (DFM). The DFM-ALD was conducted by dividing the Ru source feeding and purge steps of the conventional ALD process into four steps (shorter feeding + purge times). The DFM-ALD could efficiently eliminate the adverse effects of the Ru precursors' physisorption and byproducts during the ALD process, resulting in a more fluent ALD reaction. The physicochemical properties of the Ru films deposited via conventional ALD, DFM-ALD, and sputtering were investigated and compared in detail. The Ru films deposited via DFM-ALD showed a higher density, smoother surface morphology (Fig.1), and preferred orientation of a (101) phase compared to the conventional ALD process. Also, the Ru films grown via DFM-ALD showed higher susceptibility of oxygen atoms into the Ru films, resulting in a higher proportion of the RuO_2 layer on the Ru film surface, which is formed during the subsequent ALD process of the high-*k* TiO_2 thin film. Such a higher RuO_2 portion led to more fluent lattice-matched local epitaxial growth of the TiO_2 films with a rutile structure as well as the smoother surface morphology without local protrusions. The possible mechanism of the improved TiO_2 film growth mechanism was suggested (Fig. 2). These improvements in the physical performances also improved the electrical properties of the $Pt/TiO_2/Ru$ capacitors. A decrease in the interfacial component of equivalent oxide thickness by ~ 0.1 nm could be achieved by the DFM-ALD process compared with the cases on the sputtered Ru film. Consequently, minimum EOT values of ~0.76 nm and ~0.48 nm were obtained with enough low leakage current density ($<10^{-7}$ A/cm^2 at 0.8 V) for TiO_2 and Al-doped TiO_2 (ATO) dielectric films, respectively. The minimum EOT of 0.48 nm was comparable to the most remarkable results from the ATO/RuO_2 layers, which would have induced integration issues caused by the reduction of RuO_2. This finding indicated that the electrical performance of the high-*k* dielectric film was determined by not only the surface morphology but also the chemical properties of the underlying Ru substrate.

AA8-6 A Comparative Study on the Crystallization Behavior of Atomic Layer Deposited ZrO_2 / Y_2O_3 / ZrO_2 Dielectric Thin Films for DRAM Capacitors*, **Haengha Seo**, D. Kim, D. Kwon, J. Lim, T. Kim, H. Paik, C. Hwang,* Seoul National University, Korea (Republic of)

ZrO_2 / Al_2O_3 / ZrO_2 (ZAZ) thin films have been applied as a representative dielectric for metal-insulator-metal (MIM) capacitors in mass-produced dynamic random-access memory (DRAM) devices. However, the inserted Al_2O_3 layer required for the leakage current suppression degraded the overall crystallinity of the dielectric film, resulting in a much higher equivalent oxide thickness (EOT) compared with the undoped ZrO_2 film as the films became thinner (< 6 nm).

In this work, ZrO_2 / Y_2O_3 / ZrO_2 (ZYZ) thin films were grown on TiN (bottom) electrode by atomic layer deposition (ALD) using $Zr[N(CH_3)C_2H_5]_4$ and $Y(EtCp)_2(^iPr\text{-amd})$ as precursors. ZAZ films were also deposited in the same manner for comparison. The thicknesses of both the Y_2O_3 and Al_2O_3 layers were fixed at ~ 0.3 nm, and they were deposited on top of the ~ 2.1 nm thick ZrO_2 bottom layer. Only the top ZrO_2 layer thickness was varied between 0 and 8 nm. All samples were subjected to post-metallization annealing (PMA) at 600 °C, after TiN/Pt (top) electrode deposition.

As can be seen from **Figure 1**, the EOT of the ZrO_2 and ZYZ films showed a sudden drop at a similar physical oxide thickness (POT) of ~ 3.5 nm, whereas that of the ZAZ curve showed a similar decrease at a much greater POT (~ 6.0 nm). The result evidently indicates that the minimum POT required for the crystallization of the top ZrO_2 layer during the PMA increased significantly on the Al_2O_3 layer, while the impact of the Y_2O_3 layer on the crystallization was almost negligible.

It is noteworthy that there was another transition point in the case of the ZAZ at ~ 7 nm, which might indicate the crystallization of the bottom ZrO_2 layer. This implies that even the bottom ZrO_2 layer had not been crystallized in the thinner ZAZ case due to the presence of the Al-doping, which was not the case in ZYZ. Although the Y_2O_3 insertion layer in ZrO_2 based dielectric did not inhibit the crystallization, the leakage current was still well suppressed (2.9×10^{-8} A cm^{-2} at 0.8 V, POT ~ 6.8 nm). ZYZYZ thin films exhibited the most stable and improved leakage current control among the tested candidates.

Author Index

Bold page numbers indicate presenter

— C —
Choi, J.: AA8-1, 1
— H —
Hwang, C.: AA8-1, 1; AA8-2, 1; AA8-3, 1; AA8-6, 1
Hyun, S.: AA8-1, 1
— J —
Jeon, W.: AA8-3, 1
— K —
Kim, D.: AA8-3, 1; AA8-6, 1
Kim, H.: AA8-1, 1
Kim, T.: AA8-2, **1**; AA8-3, 1; AA8-6, 1
Kwon, D.: AA8-3, **1**; AA8-6, 1
— L —
Lee, H.: AA8-1, 1
Lim, J.: AA8-3, 1; AA8-6, 1
— P —
Paik, H.: AA8-6, 1
— S —
Seo, H.: AA8-3, 1; AA8-6, **1**
— W —
Wang, B.: AA8-1, **1**