Chemical Vapor Deposition of Ru Thin Films with an Enhanced Morphology, Thermal Stability, and Electrical Properties Using a RuO4 Precursor

Jeong Hwan Han,[†] Sang Woon Lee,[†] Gyu-Jin Choi,[†]
Sang Young Lee,[†] Cheol Seong Hwang,*,[†]
Christian Dussarrat,[‡] and Julien Gatineau[‡]

*Department of Materials Science and Engineering and
Inter-university Semiconductor Research Center, Seoul
National University, Seoul 151−744, Korea, and Air Liquide
Laboratories, 28 Wadai, Tsukuba-Shi,
Ibaraki 300−4247, Japan*

Ru thin films were grown on Si, SiO2, and TiN substrates by pulsed chemical vapor deposition using RuO4 and 5% H2/95% N2 as the precursor and reducing gas, respectively, at temperatures ranging from 190 to 350 °C. A high growth rate of 0.18 nm/pulse, (0.43 nm/min), a low impurity concentration, and a very smooth surface were achieved at a substrate temperature of 230 °C. The films showed an excellent thermal stability up to 800 °C. TiO2 films grown on these Ru films showed superior electrical performance (higher capacitance and lower leakage current) to those deposited on Ru films deposited by other methods.

The deposition of Ru thin films, either by metal-organic chemical vapor deposition (MOCVD) or atomic-layer-deposition (ALD), has been studied extensively using a variety of metal-organic (MO) precursors for applications in capacitors for dynamic random access memory (DRAM) using high-dielectric TiO2 or SrTiO3 films.[1−7] Although ALD processes produce conformal deposition of thin Ru films with uniform microstructures on severe three-dimensional structures,[2] the low saturation growth rate (∼0.03 nm/cycle), long incubation period, surface-sensitive growth and insufficient thermal stability are major hurdles for its application to DRAM capacitors.[2] Because most ALD processes for Ru films proceed using a MO precursor and oxygen gas as the reducing agent, Ru films deposited using these methods generally contain carbon and oxygen impurities. This results in insufficient thermal stability and adverse interference with the electrical performance of the dielectric films grown on

top. In addition, the low growth rate of the ALD process is a serious concern because of the extremely high cost of Ru precursors. Therefore, this study examined Ru film deposition using an inorganic RuO4 precursor and H2(5%)/N2(95%) reduction gas at growth temperatures ranging from 190 to 350 °C. Although the ALD-type growth process was initially attempted, this precursor decomposed thermally at all temperatures tested, which made it a pulse-CVD type process. This is a different behavior from the previously reported CVD/ALD results using the same precursor.[8] However, the film produced showed an extremely low surface roughness and excellent thermal stability, which improved the electrical performance of TiO2 films deposited on top compared with those grown on other ALD or even sputtered Ru films. In addition, the growth rate was much higher than its ALD counterpart but the three-dimensional conformality was still confirmed.

Ru films were deposited using an 8 in. diameter wafer scale shower-head type CVD/ALD reactor (Quros. Co., Plus-200) in pulse CVD (p-CVD) mode. The RuO4 precursor was dissolved in an ethyl-methyl-fluorinated solvent mixture (ToRuS, produced by Air Liquide Co.[8] with a density of 0.6 M,), which has an identical vapor pressure to that of the RuO4. The ToRuS blend was obtained by adding dissolved RuO4 in a blend of chosen organic solvent. Therefore, a standard bubbling technique was used. Use of solvent elevates the safety concern of pure RuO4 precursor and helps the proper control of the growth process. No carrier gas was used. The precursor solution temperature was maintained at 3 °C. The chamber wall temperature and deposition pressure were 50 °C and 3.5−4 Torr, respectively. The substrates were (noncleaned) Si, thermally grown 100 nm thick SiO2 and sputtered TiN. The precursor and reactant pulse sequence, which consisted of a single deposition cycle, was a 3 s precursor pulse−7 s Ar gas (600 standard cubic centimeter per min (sccm)) purge−10s H2(5%)/N2(95%) gas pulse (1000 sccm)−5s Ar gas (600 sccm) purge. The film thickness was measured by field-emission scanning electron microscopy (FESEM) and X-ray reflectivity (XRR). The area density of the Ru films was measured by X-ray fluorescence spectroscopy (XRF). The bulk density was also examined by XRR. The sheet resistance of the Ru thin films was measured at room temperature using a four-point probe. The crystalline structure of the Ru thin films was investigated by X-ray diffraction (XRD) using Cu Kα radiation. The relative impurity (oxygen, carbon, and fluorine) content in the films was investigated by secondary ion mass spectroscopy (SIMS), and the surface morphology and roughness was examined by atomic force microscopy (AFM, AFM scan area was $2 \times 2 \ \mu m^2$) and SEM. The thermal stability was tested by postdeposition annealing (PDA) at temperatures ranging from 400 to 1000 °C by a rapid thermal annealing (RTA) under a N2 atmosphere for 1 min. For comparison, Ru films with a similar thickness were grown by ALD at 250 °C

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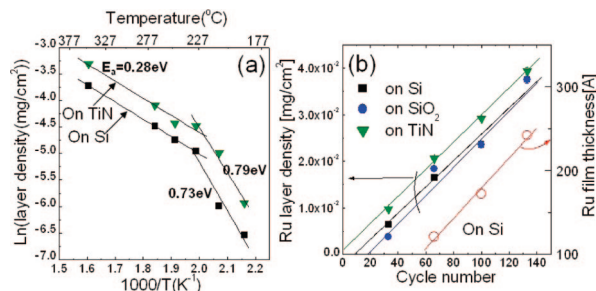(8) Gatineau, J.; Yanagita, K.; Dussarrat, C. *Microelectron. Eng.* **2006**, *83*, 2248.

Figure 1. (a) Arrhenius plot of the variations in the Ln (area density) of a Ru film deposited on Si and TiN substrate as a function of the reciprocal substrate temperature in Kelvin, and (b) change in the layer density and thickness of the Ru films grown on the Si, SiO$_2$, and TiN substrates as a function of the number of deposition cycles.

Figure 2. (a) SIMS depth profile results of the as-deposited ALD Ru (upper panel) and p-CVD Ru (lower panel) films, and (b) $\theta-2\theta$ XRD patterns of the ~20 nm thick p-CVD, ALD, and s-Ru films at the as-grown state and after the RTA at 700 and 900 °C.

Figure 3. (a) Root-mean-squared (rms) roughness of a 20 nm thick Ru films (inset: AFM images of the as deposited films, data were collected from 2 × 2 μm^2), and (b) upper panel, AFM surface micrographs of the Ru films (on Si substrate) after the RTA at 800 °C and lower panel, SEM images after the RTA at 700 °C. Data in (a) were collected from the area excluding the large holes shown in lower right panel of (b).

(ALD-Ru film) using a previously reported method.[2] To confirm the electrical properties of the dielectric films, TiO$_2$ thin films were grown on the p-CVD Ru, ALD-Ru, and sputtered (s-Ru) Ru films using a previously reported ALD process at 250 °C.[9,10] The dielectric performance of the TiO$_2$ films on the various Ru films was investigated using an e-beam evaporated Pt top electrode through a metal shadow mask (0.3 mm in diameter of holes).

Figure 1 (a) shows an Arrhenius plot of Ln (area density) of a Ru film deposited on Si and TiN substrate as a function of the reciprocal substrate temperature in Kelvin (T_s). This shows the typical growth behavior of CVD on both substrates, where high and low T_s dependencies were obtained in the low and high temperature regions ($T_s \lesssim 230$ °C and $\gtrsim 230$ °C) with activation energies of ~0.75 and ~0.28 eV, respectively. The low and high T_s regions correspond to the surface-chemical reaction and gas-phase diffusion controlled growth regions, respectively. If it was in ALD mode, the temperature dependency should have been reversed or T_s-independent growth should have been observed in a certain T_s region. The generally higher growth rate of Ru film on the TiN substrate compared to that on Si substrate was attributed to the lower incubation period of Ru film growth. Figure 1b shows the change in the layer density and thickness of Ru films grown on the Si, SiO$_2$ and TiN substrates as a function of the number of deposition cycles (n_{cy}). Growth showed a linear behavior in the n_{cy} range investigated, and the slope corresponded to the layer density and thickness growth rates of 283 ng/(cycle cm^2) and 0.18 nm/cycle, respectively. Because a single deposition cycle takes 25 s, this growth rate corresponds to 0.43 nm/min, which is more than 6 times higher than the growth rate for typical ALD processes using Ru(EtCp)$_2$ and Ru(DMPD)(EtCp). There were certain initial nongrowing cycles (incubation cycles) for the cases of Si and SiO$_2$ substrates but there was almost no incubation cycles on TiN. The incubation periods for the p-CVD Ru on Si and SiO$_2$ substrates were smaller than that of the ALD Ru film.

Figure 2a shows the SIMS depth profile of the 25 nm thick p-CVD Ru and ALD Ru films. Although quantification of the impurity concentration was not possible by SIMS because
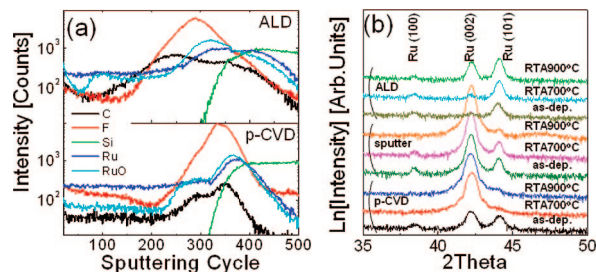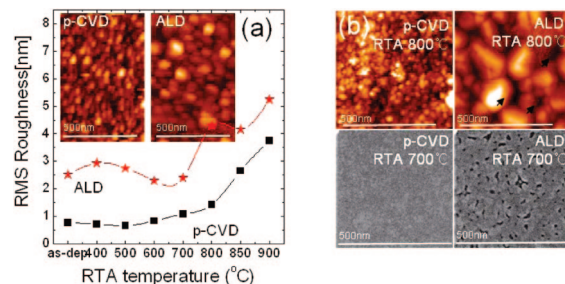
of the matrix effect, it is clear that the p-CVD Ru film contains lower impurity content (C and RuO) than the ALD Ru film. H content was also lower, although data was not shown for clarity. Elemental O signal was very weak in this SIMS. Fluorine was also detected by the solvent effect but its concentration should be far lower than 1% because Auger electron spectroscopy was not able to detect any fluorine. Fluorine was also detected with a smaller content from the ALD-Ru film due to the residual fluorine in the reaction chamber. Figure 2b shows the XRD patterns in $\theta-2\theta$ mode of the p-CVD, ALD Ru, and s-Ru films before PDA and after the PDA at 700 and 900 °C, respectively. XRD showed that the as-deposited films were crystalline. The preferred growth direction of the as-deposited p-CVD Ru film was almost identical to that of the s-Ru film but the ALD Ru film showed a different preferred growth direction. There was an increase in the (002) XRD peak intensity of the p-CVD Ru and the s-Ru films after PDA but the (100) and (101) peaks became weakened. The ALD Ru film still showed an appreciable intensity of (101) peak even after the RTA at 900 °C. The p-CVD Ru film showed the most highly (002) oriented behavior after the RTA at 900 °C. The resistivity of the as-deposited films was ~20 $\mu\Omega$ cm. XRR showed that the film densities are similar (12.0 g cm^{-3} for p-CVD and ALD Ru films. Bulk Ru density is 12.3 g cm^{-3}).

Figure 3a shows the changes in the root-mean-squared (rms) roughness of the 20 nm thick p-CVD and ALD Ru films (on Si substrate), respectively, as a function of the RTA temperature. The p-CVD Ru film showed a smaller rms roughness at the as-deposited state compared with the ALD Ru film. This is due to the smaller grain size of the p-CVD film compared with that of the ALD Ru film (inset AFM

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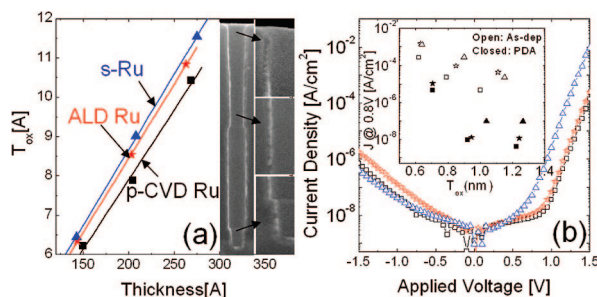
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Figure 4. (a) Changes in t_{ox} as a function of the ALD TiO_2 film thickness grown on the p-CVD-Ru, ALD-Ru, and s-Ru, and (b) $J-V$ curves of the ~23 nm thick TiO_2 film on the various Ru films. The inset figures in (a) shows SEM micrographs of the p-CVD Ru film on a capacitor hole structure formed in CVD SiO_2 with a opening diameter of 100 nm and a depth of 1000 nm, and inset in (b) shows the changes in the J (at 0.8V) of the TiO_2 films as a function of the t_{ox} values on the three Ru electrodes.

figures). The small rms roughness value of the p-CVD Ru film was maintained up to 800 °C whereas the ALD Ru film showed a large increase in roughness at the same temperature. AFM *(SEM)* images of the two films annealed at 800 °C (700 °C) (Figure 3b) clearly show the different thermal stability of the two films. The ALD Ru films revealed the formation of many voids (indicated by black arrows) due to excessive grain growth, but the p-CVD film showed slight grain growth without forming any voids. This suggests superior thermal stability of the p-CVD Ru film to that of the ALD Ru film, which improved the electrical properties of the dielectric films grown on top.

The three-dimensional conformality of the film on a capacitor hole structure formed by CVD SiO_2 with an opening diameter of 100 nm and a depth of 1000 nm was confirmed to be ≳90% (thickness ratio between the top and bottom corners), as shown in the inset of Figure 4a.

Figure 4a shows the change in the equivalent oxide thickness ($t_{ox} = t_{phy}(k_{SiO_2}/k_{TiO_2})$, where t_{phy}, k_{TiO_2}, and k_{SiO_2} are the physical thickness and dielectric constants of TiO_2 and SiO_2, respectively, as a function of the ALD TiO_2 film thickness grown on the p-CVD-Ru, ALD-Ru, and s-Ru. The t_{ox} values of the TiO_2 films were generally smaller at a given t_{phy}, and k_{TiO2}, which was calculated from the slope of the line of best fit, is slightly larger on the p-CVD Ru film. Because the TiO_2 has a tetragonal rutile structure on Ru films,[9,10] the k_{TiO_2} values were 100–110. The k_{TiO_2} value is anisotropic according to the different crystallographic axes, so that the slightly different k_{TiO_2} values of the films on the different Ru electrodes might be due to the different preferred growth directions of the TiO_2 films. However, the difference between k_{TiO_2} values on the ALD Ru and s-Ru film was small whereas there was a significant difference in the Ru orientations (XRD patterns in Figure 2b). Therefore, it is unclear if the film orientation really affects the k_{TiO_2} value. However,

the y-axis intercept, which reflects the presence of an interface layer, was the smallest for the case of p-CVD Ru electrode. This suggests that the adverse interfacial effect was minimized for the p-CVD Ru case because of its chemical purity and stability. Furthermore, the leakage current vs voltage ($J-V$) performance of the TiO_2 film on the p-CVD Ru film was improved considerably compared with the cases on the other Ru films.

Figure 4b shows the $J-V$ curves of the TiO_2 films on various Ru films with similar t_{ox} values (0.92–1.03 nm) after cure annealing of the Pt top electrode at 400 °C. The J level of the TiO_2 film on the p-CVD Ru film was much lower than the others, even though the t_{ox} value of this film was smallest. The inset figure in Figure 4b shows the variations in the J (at 0.8V) of the TiO_2 films as a function of the t_{ox} values on the three Ru electrodes. It can be understood that the TiO_2 films on the p-CVD Ru films show the smallest J level at a given t_{ox} value before and after cure annealing.

Because of the high work functions of the Pt and RuO_2 electrodes and the n-type nature of the undoped TiO_2 films, both interfaces must form a Schottky barrier for electron injection.[10] The lower J on the p-CVD Ru film suggests that the Schottky barrier height for this case was higher than the others. It was reported that thermally stable electrodes are essential for the low J of titanate dielectric films.[11] Therefore, the improved thermal stability, smoother surface and chemical purity of the p-CVD Ru electrode largely improved the $J-V$ performance of the TiO_2 dielectric film grown on top. This is another crucial merit of this film as a capacitor electrode in future DRAMs.

In summary, Ru thin films were grown on Si, SiO_2, and TiN substrates by pulse CVD using RuO_4 and H_2/N_2 mixture gas as the Ru precursor and reactant, respectively, at temperatures ranging from 190 to 350 °C. The Ru film grown at 230 °C showed a higher growth rate of 0.18 nm/cycle and excellent thermal stability up to 800 °C because of its very low impurity concentration. The electrical properties of the ALD TiO_2 films grown on top of the p-CVD Ru films are considerably improved compared with the cases on ALD Ru and even sputtered Ru. Along with the sufficient step coverage, the Ru films deposited using the present technique show significant improvements in the device properties compared with films deposited using other methods, and are expected to find applications in the next generation DRAM capacitors.

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