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Growth of highly conformal ruthenium-oxide thin films with enhanced nucleation by atomic layer deposition

Ji-Yoon Park<sup>\*</sup>, Seungmin Yeo<sup>\*</sup>, Taehoon Cheon<sup>\*</sup>, <sup>+</sup>, Soo-Hyun Kim, <sup>\*,\*</sup>, Min-Kyu Kim<sup>×</sup>,

*Hyungjun Kim<sup>×</sup>*, *Tae Eun Hong*<sup>I</sup>, *and Do-Joong Lee*<sup>#</sup>

\*School of Materials Science and Engineering, Yeungnam Universitsy, Gyeongsan-si 712-749, Korea

<sup>+</sup>Center for Core Research Facilities, Daegu Gyeongbuk Institute of Science & Technology, Dalseong-gun, Daegu, 711-873, Korea

<sup>×</sup>School of Electrical and Electronic Engineering, Yonsei University, Seoul, 120-749, Korea
 <sup>I</sup>Busan Center, Korea Basic Science Institute, 1275 Jisadong, Gangseogu, Busan, 618-230, Korea

<sup>#</sup>School of Engineering, Brown University, Providence, RI 02912, United States

### ABSTRACT

Highly conformal and conductive RuO<sub>2</sub> thin films were deposited without nucleation delay using atomic layer deposition (ALD) by zero-valent metallorganic precursor, (ethylbenzyl)(1,3-cyclohexadienyl)Ru(0) (EBCHDRu,  $C_{14}H_{18}Ru$ ) and molecular oxygen (O<sub>2</sub>) as a precursor and reactant, respectively. RuO<sub>2</sub> thin films could be successfully prepared by controlling the process parameters, such as a reactant flow rate, a reactant pulsing time, a precursor pulsing time, and a deposition temperature. X-ray diffractometry, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry analysis revealed that the formation of a RuO<sub>2</sub> phase became favorable with increasing both the reactant flow rate and the pulsing time and with decreasing the precursor pulsing time and the deposition temperature. With the optimized pulsing conditions, the RuO<sub>2</sub> film deposited at 225 °C had a tetragonal structure and exhibited excellent properties such as the low resistivity of 118  $\mu\Omega$ -cm, the high density of 6.85 g/cm<sup>3</sup> close to the bulk value, and the negligible roughness of 0.33 nm. The growth rate of ALD-RuO<sub>2</sub> was as high as 0.186 nm/cycle on the SiO<sub>2</sub> substrate and the number of incubation cycles was negligible as 2. The film showed excellent step coverage of ~ 100 % onto 25-nm-width trench structures with an aspect ratio of 4.5. The ALD-RuO<sub>2</sub> was highly stable up to annealing at 700 °C in both O2 and N2 ambient. Finally, the ALD-RuO2 film was evaluated as a bottom electrode of a metal-insulator-metal capacitor with a high-k (dielectric constant) ALD-TiO<sub>2</sub> dielectric. The dielectric constant of ALD-TiO<sub>2</sub> was confirmed to be as high as ~ 68. This extremely high dielectric constant was attributed to the formation of a rutile-structured TiO<sub>2</sub> film on top of the ALD-RuO<sub>2</sub> bottom electrode, as evidenced by high-resolution transmission electron microscopy analysis.

#### I. Introduction

Ever-shrinking dimensions of dynamic random access memory (DRAM) cells with increasing a packing density have made a capacitor size increasingly smaller and smaller. Corresponding with this, the capacitor with an insulator possessing extremely low leakage current and high dielectric constant becomes more important. For example, capacitors with various TiO<sub>2</sub>-based high-*k* (dielectric constant) dielectric films, such as TiO<sub>2</sub>, Al-doped TiO<sub>2</sub>, SrTiO<sub>3</sub>, (Ba,Sr)TiO<sub>3</sub>, and Ta<sub>2</sub>O<sub>5</sub> have been extensively studied [1-12]. For fabrication of a reliable and high capacitordensity devices, a selection of electrodes compatible with high-*k* dielectrics becomes extremely important and a MIM (metal-insulator-metal) capacitor could be a viable solution to address the continuous scaling down of the DRAM capacitor [12]. In the view of electrode materials of MIM capacitors, Ru (ruthenium) and RuO<sub>2</sub> have drawn much attention recently. They have excellent properties, such as good susceptibility to dry etching, low resistivity (Ru:  $\sim$ 7 IIcm and RuO<sub>2</sub>:

~46  $\square$ cm), high chemical stability and high work function (Ru: 4.7 eV and RuO<sub>2</sub>: 5.1 eV) compared to a currently used TiN electrode (~4.2 eV) [13]. In particular, because a high work function of the metal electrode is favorable for suppression of a leakage current, RuO<sub>2</sub> can hold a clear advantage even compared to Ru [8]. For meeting requirements of the high-performance devices with the ever-shrinking dimensions, a technique which guarantees a conformal deposition onto high aspect-ratio trench or hole structures with excellent thickness uniformity and process controllability is highly demanded. In these respects, atomic layer deposition (ALD) for these materials have drawn much attention because ALD uses a self-limited film growth mode by a surface-saturated reaction of precursors and reactants, which enables an atomic scale control of the film thickness with excellent step coverage [14, 15].

Previously, ALD-RuO<sub>2</sub> thin films have been deposited by various precursors such as bis(cyclopentadienyl) Ru(II) [RuCp<sub>2</sub>, Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] [16], bis(ethylcyclopentadienyl) Ru(II) [Ru(EtCp)<sub>2</sub>, Ru(C<sub>5</sub>H<sub>5</sub>C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] [17 ~ 22], bis(2,2,6,6-tetramethyl-3,5-heptanedinonato)(1,5-cyclooctadiene) Ru(III) [Ru(thd)<sub>2</sub>(cod)] [23] and (methylcyclopentadienyl)(Pyrrolyl) Ru(II) [MeCpPyRu] [24]. Here, the metal valence of these precursors is 2 or 3 and O<sub>2</sub> molecules have been generally used as a reactant. By using the same reaction scheme, ALD-Ru as well as ALD-RuO<sub>2</sub> could be deposited by controlling process parameters [17 ~ 20].

In addition to the high conformality of the electrode materials, a process to guarantee the thinnest and continuous electrode films for a reliable MIM capacitor is becoming essential with the device scaling-down. However, previous results suggested that the ALD-RuO<sub>2</sub> processes with these precursors and O<sub>2</sub> reactant showed a relatively long incubation cycles with a considerably lower film growth rate at the initial stages of film deposition [18, 21, 24, 25], which is related to the delayed nucleation of the film material. The incubation cycles of the ALD-RuO<sub>2</sub> process at 265 °C using the Ru(II)(EtCp)<sub>2</sub> precursor and O<sub>2</sub> reactant were as high as ~35, which is calculated from the linear extrapolation of the thicknesses to the numbers of ALD cycles [18]. Kim et al. [25] reported that the incubation cycles of ALD-RuO<sub>2</sub> process using the Ru(II)(EtCp)<sub>2</sub> precursor were dependent on the substrate, which were 45 and 13 cycles on SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> substrate, respectively. Salaün et al. [21] reported that the ALD-RuO<sub>2</sub> film deposited at 280 °C was not continuous on a thermally grown SiO2 even after 700 ALD cycles using the same precursor, and the continuous film was obtained after 1200 ALD cycles. The nucleation delays shown in the ALD-RuO<sub>2</sub> processes have also been reported in ALD-Ru processes using the same chemistry. For example, Yim et al.[26] and Kukli et al.[27] reported that the ALD-Ru film deposited above 300 °C was not continuous on the SiO<sub>2</sub> even after 500 and 100 ALD cycles

using cyclopentadienyl-based precursors,  $Ru(II)(EtCp)_2$  and (EtCpPy)Ru(II) precursors, respectively, with O<sub>2</sub> as a reactant. Using another cyclopentadienyl-based precursor,  $Ru(II)(Cp)_2$ [28], the incubation cycles of ALD-Ru was above 500 cycles. The poor nucleation of the ALD-Ru process was also found when  $\beta$ -diketonate Ru(III) precursor was used [29]. The retarded nucleation with significantly long incubation cycles will lead to a rough morphology of the film which is unsuitable for the conformal film deposition onto high aspect-ratio structures. The issues of the nucleation will become more significant with decreasing the device sizes. In this respect, a high initial nuclei density is essential to achieve continuity of ultra-thin ALD-RuO<sub>2</sub> films.

Recent investigations by us showed that the nucleation of ALD-Ru process was enhanced considerably using several zero metal valence precursors, such as isopropyl-methylbenzene-(IMBCHDRu,  $C_{16}H_{22}Ru$ ), cyclohexadiene Ru(0)(ethylbenzyl) (1-ethyl-1,4cyclohexadienyl)Ru(0), and (EBECHDRu,  $C_{16}H_{22}Ru$ ), (ethylbenzen)(1,3-cyclohexadiene)Ru(0)(EBCHDRu,  $C_{14}H_{18}Ru$  and  $O_2[30 \sim 32]$ , compared to the precursors with higher metal valences. There was negligible and no incubation cycle for the ALD-Ru film growth on the covalent SiO<sub>2</sub> and ionic TiN substrates, respectively. Due to the enhanced nucleation, the ALD-Ru films deposited with zero metal valence precursors showed an excellent conformality with a smooth surface. In this study, we investigated the ALD-RuO<sub>2</sub> process using a zero metal valence Ru metallorganic precursor, EBCHDRu and O<sub>2</sub> reactant. By controlling the process parameters, such as precursor and reactant pulsing conditions, and deposition temperature, we could successfully prepare the ALD-RuO<sub>2</sub> thin films with negligible incubation cycles and perfect step coverage at extremely-narrow nano-sized (25 nm in width) trenches. Such the developed ALD-RuO<sub>2</sub> film

has been applied as a bottom electrode of a MIM capacitor with an ALD-grown high-k TiO<sub>2</sub> dielectric.

#### **II. Experiments**

Deposition - The films were deposited using a traveling wave-type thermal ALD reactor (Lucida-D100, NCD Technology, Korea) with the zero valence EBCHDRu as a precursor. Detailed description of the precursor can be found elsewhere [32]. The deposition temperature was varied between 185 and 270 °C and the typical deposition temperature was 225 °C at a deposition pressure of 1 Torr. P-type Si (100) wafers covered with 100-nm-thick thermally grown SiO<sub>2</sub> were used as substrates. The Ru precursor was vaporized in a bubbler at an elevated temperature of 100  $^{\circ}$ C and was carried into the process chamber with N<sub>2</sub> gas flow rate of 100 standard cubic centimeters per minute (SCCM). The line temperature for the precursor delivery was kept at 140 °C to prevent condensation of the precursor. As a reactant, the O<sub>2</sub> gas diluted with N<sub>2</sub> gas was flown into the chamber. The ratio of O<sub>2</sub> versus total gas (N<sub>2</sub>+O<sub>2</sub>) flow rates (fO<sub>2</sub>/N<sub>2</sub>+O<sub>2</sub>) was varied from 20 (O<sub>2</sub>: 40 SCCM with N<sub>2</sub>: 160 SCCM) to 100 % (O<sub>2</sub> 200 SCCM without N<sub>2</sub>) with keeping the total amount of gas flow rate to 200 SCCM. Between the precursor pulsing and the reactant pulsing, a purging process was done with N<sub>2</sub> gas of 200 SCCM during 10 s; the sequence of precursor pulsing, purging, reactant pulsing and then purging occurs in each ALD cycle.

Analysis of film properties - For phase and crystallinity identification, grazing-incidence angle (incident angle,  $\theta = 3^{\circ}$ ) X-ray diffractometry (GIAXRD, PANalytical X'-pert MRD with Cu-K<sub>\alpha</sub> radiation at 1.5 kW) analysis was performed. The thicknesses of the films were determined from X-ray reflectance (XRR, PANalytical X'-pert MRD with Cu-K<sub> $\alpha$ </sub> radiation at 1.5 kW). Its resistivity was determined by combining the sheet resistance of the film measured by four-point probe and the measured thickness. The chemical compositions of the films were analyzed by secondary ion mass spectrometry (SIMS, CAMECA IMS-6f installed in Korea Basic Science Institute) with a 1.5 keV Cs<sup>+</sup> beam. Rutherford backscattering spectrometry (RBS) was performed to calibrate the SIMS results. The chemical bindings of the films were analyzed by using X-ray photoelectron spectroscopy (XPS). Plan-view transmission electron microscopy (TEM, Tecnai F20 equipped with 200 kV accelerating voltage and field emission gun) was used for the analysis of the nucleation at the initial stage of films growth. TEM images were taken digitally using a 2k '2k (2048 pixel 'pixel) charge coupled device (CCD) camera (Gatan UltraScan<sup>TM</sup> 2000). Step coverages of the films were evaluated at the trench with the aspect ratio (AR) of ~ 4.5 (top opening width: ~ 25 nm).

*Evaluation as a bottom electrode of MIM capacitor* - ALD-RuO<sub>2</sub> were evaluated as a bottom electrode in a MIM structure with high-*k* ALD-TiO<sub>2</sub> dielectric. Here, ALD-TiO<sub>2</sub> film with the 10 nm in thickness was deposited using tetrakis-dimethyl-amino-titanium (TDMAT) as a precursor at the deposition temperature of 250 °C. O<sub>2</sub> plasma was used as a reactant. MIM capacitors were fabricated by depositing 60 nm-thick Ru films atop the ALD-TiO<sub>2</sub> using sputtering through a shadow mask for the top electrode and these capacitors were annealed at 400 °C under an N<sub>2</sub>

atmosphere for 10 minutes to reduce trap charge densities after fabrication of the top electrodes. A Hewlett-Packard 4194A impedance analyzer was used to measure the capacitance-voltage (C-V) of the MIM capacitors.

#### **III. Results and Discussion**

### A. Optimization of deposition parameters for growth of ALD-ruthenium oxide films

In the previously study, we investigated the ALD-Ru process using the same reaction chemistry [32]. A self-limited film growth was confirmed at the deposition temperature of 225 °C and the growth rate was 0.1 nm/cycle on the SiO<sub>2</sub> substrate with a negligible number of incubation cycles (approximately 3 cycles). The basic pulsing condition for the ALD-Ru process was precursor pulsing for 5 s, precursor purging for 10 s, reactant pulsing for 1 s, and reactant purging for 10 s and the same condition was firstly used to deposit ALD Ru oxide films. For the deposition of pure Ru film, the reactant O<sub>2</sub> molecules were diluted with N<sub>2</sub> molecules and the ratio of O<sub>2</sub> flow rate versus total gas (O<sub>2</sub> + N<sub>2</sub>) flow rate was 20 %. In this study, we increased the O<sub>2</sub> flow rate from 40 to 200 SCCM with keeping the total amount of gas (O<sub>2</sub> + N<sub>2</sub>) flow rate to 200 SCCM.

Figure 1 (a) showed the resistivities of the films deposited on the thermally grown SiO<sub>2</sub> surfaces as a function of the ratio of the reactant flow rates  $[O_2/(O_2+N_2)]$  under the given pulsing

condition (5s-10s-1s-10s). The resistivity of the film deposited with the reactant ratio of 20 % was ~ 22  $\mu\Omega$  cm, as corresponds to that of pure Ru [32], and it continuously increased with increasing the reactant ratio. The resistivity of the film deposited with 100% reactant ratio (providing O<sub>2</sub> molecules only) was ~ 52  $\mu\Omega$  cm. Figure 1 (b) showed the GIAXRD results of the films shown in Fig. 1 (a). With increasing the O<sub>2</sub> flow rate, the crystallinity of Ru film was improved as evidenced by the increase of the X-ray intensities from hexagonal-close-packed (HCP)-Ru. One could not find the XRD peaks related to a RuO<sub>2</sub> phase. Considering the resistivity of the metal film is generally decreased as the film crystallinity is improved, the XRD results of the ALD-Ru films as a function of the reactant ratio are seems to be strange. Though, when the reactant gas ratio was 100 %, the X-ray intensity from HCP-Ru was rather decreased and a closer look on the XRD results confirmed the very tiny peaks at  $2D = \sim 28^{\circ}$  and  $\sim 35^{\circ}$ , which could be identified to tetragonal  $RuO_2$  (110) and (101). Thus, it could be thought the oxygen might incorporate into the film by increasing the O<sub>2</sub> flow rate in the reactant pulsing step, which partly can explain the increase in the resistivity as shown in Fig. 1 (a). It was reported that the resistivity of ALD-Ru films deposited using Ru(II)(EtCp)<sub>2</sub> precursor increased abruptly at a certain point of a reactant ratio [O<sub>2</sub>/(Ar + O<sub>2</sub>)] and it was mainly attributed to the formation of RuO<sub>2</sub>[17, 19, 20]. Not correspondingly, the other report using Ru(II)(Cp)<sub>2</sub> precursor showed that the resistivity monotonically increased with increasing the flow rate of O<sub>2</sub> flow without the formation of RuO<sub>2</sub> [16], similar to the results obtained in this study.

To further confirm effects of deposition conditions on the incorporation of oxygen into Ru and the formation of RuO<sub>2</sub>, the pulsing time of the reactant was increased up to 60 s while keeping the gas flow rate ratio of 100 % (200 SCCM  $O_2$  without  $N_2$ ). Figure 2 (a) showed the resistivity of the films deposited at 225 °C as a function of the reactant pulsing time. Here, the precursor

pulsing time was fixed to 5 s. The resistivity of the films monotonically increased with increasing the reactant pulsing time, as similar to the Fig. 1(a), and it was around ~ 118  $\mu\Omega$  cm when the reactant pulsing time was 60 s (the longest time used in this study). The corresponding XRD results were shown in Fig. 2 (b). When the reactant pulsing time was increased from 1 to 10 s, the changes in the XRD peaks were clearly shown. The intensities of XRD peaks at  $2D = \sim$ 38° and ~ 44°, which could be identified to the hexagonal Ru, decreased. Instead, the XRD peaks originated from the tetragonal RuO<sub>2</sub> were clearly appeared at at  $2\mathbb{I} = \sim 28^{\circ}$  and  $\sim 35^{\circ}$ , indicating the formation of RuO<sub>2</sub> phase. When the reactant pulsing time was increased to 30 s, the peaks intensities from RuO<sub>2</sub> became stronger while those from Ru became weaker. Finally, with the reactant pulsing time of 60 s, the peaks intensities from RuO<sub>2</sub> were further increased and the very tiny peaks from Ru were identified, indicating that the most of the film consisted of the RuO<sub>2</sub> phase. The volume fraction of RuO<sub>2</sub> could be calculated from the areal ratio of the XRD peaks related to the Ru and RuO<sub>2</sub> phases. The XRD analysis also clarified that the increase of the resistivity with increasing the O<sub>2</sub> pulsing time shown in Fig. 2 (a) was due to the formation of the RuO<sub>2</sub> phase.

XPS was performed on the films deposited with various reactant pulsing condition to examine the bonding status of Ru. The XPS data was obtained after sputtering an approximately 4-nmthick film to eliminate surface carbon contamination and to characterize the bonding status of the film itself. The XPS data was calibrated with the adventitious C *1s* peak (284.5 eV) detected on the film surface. Figure 3 showed the binding energies of Ru *3d* core electrons of the films. In the case of a pure ALD-Ru film deposited with the reactant pulsing time of 1 s and the gas flow ratio of 20 %, Ru peak was composed of two well-resolved peaks, 280.26 eV for Ru *3d*<sub>5/2</sub> and 284.44 eV for Ru *3d*<sub>3/2</sub>. Even though the XPS peak of Ru *3d*<sub>3/2</sub> at 284.44 eV overlaps with the C

*Is* primary peak at 284.5 eV, the RBS results indicated that the carbon content in the films was negligible, as will be addressed in the following paragraph. Thus, the peaks in Fig. 3 (a) can be considered as those of the Ru-Ru bonding in the film. The figs. 3 (b)-(f) showed the XPS results of the films deposited with the gas ratio of 100 %. In the case of both the film deposited with the same reactant pulsing time for ALD-Ru deposition (1 s) [Fig. 3 (b)] and that deposited with the increased reactant pulsing time of 10 s [Fig. 3 (c)], the changes in XPS results on Ru 3d photoelectrons were not significant as compared with that of the pure ALD-Ru film. But, a careful investigation on the XPS results of the film deposited with the reactant pulsing time of 10 s [Fig. 3 (c)] showed that the peak intensity from the Ru-Ru bonding was slightly decreased and the peaks were slightly extended to higher binding energies, which was owing to the appearance of the RuO<sub>2</sub> bonding. This indicated that the RuO<sub>2</sub> phase started to be formed as same as the XRD results in Fig. 2 (b). The changes of the XPS peaks with increasing the reactant pulsing time was more apparently shown in the sample deposited with the reactant pulsing time of 30 s [Fig. 3 (d)]. With further increasing the reactant pulsing time to 60 s [Fig. 3 (e)], the peak intensity from the Ru-Ru bonding was significantly decreased and the film was mostly composed of the RuO<sub>2</sub> bonding.

Figure 4 showed the XPS O *1s* spectrum of the films as a function of the reactant pulsing time. In the case of the pure Ru film (deposited with the reactant pulsing time of 1 s and the gas flow ratio of 20 %) [Fig. 4(a)], it is very difficult to find any specific peak of O *1s* related to the RuO<sub>2</sub> bonding, indicating the negligible amount of oxygen and the film is composed of almost pure Ru. The figures 4 (b)-(e) showed the XPS results of the films deposited with the gas ratio of 100 %. In the case of the sample deposited with the reactant pulsing time of 1 s, the O *1s* peak related to the RuO<sub>2</sub> bonding started to be detected, supporting the formation of small amount of the RuO<sub>2</sub>

phase, as observed in the XRD analysis [Fig. 2(b)]. With further increasing the reactant pulsing time up to 60s, the intensity of the O Is peak continuously increased. For the sample deposited with the reactant pulsing time above 30 s, O Is peak related to the RuO<sub>3</sub> phase was also developed as well as the intensity of O Is peak related to the RuO<sub>2</sub> bonding was increased, indicating the increase of the oxygen content in the film. Thus, both the XRD and XPS results showed that both the pure Ru and the RuO<sub>2</sub> could be controllably grown by changing the deposition parameters.

Figure 5 showed the RBS spectra (incident energy of He<sup>++</sup> is 2 MeV) of the film with the reactant pulsing time of 60 s. The backscattering signal from O in the deposited film was clearly observed. By using the RUMP simulation, the ratio of O and Ru (O/Ru) was determined as 1.55, which is relatively less oxygen content as compared to O/Ru ratio of the stoichiometric RuO<sub>2</sub>. This could be understood from the existence of the small amount of Ru as observed in the very tiny peaks of the XRD results. Figure 5 (b) showed the ratio of O and Ru (O/Ru) in the films as a function of the reactant pulsing time, which was estimated based on the SIMS depth profile. Here, the SIMS results were calibrated with those of the RBS analysis. As expected, the O/Ru ratio in the film increased with increasing the reactant pulsing time.

Upon the optimized reactant pulsing conditions for RuO<sub>2</sub> deposition (the reactant pulsing time of 60 s and the gas flow ratio of 100%), effects of a precursor pulsing time have been examined. Figure 6 (a) showed the resistivities of the films as a function of precursor pulsing time. When the precursor pulsing time increased to 1 s from 5 s (the condition used above), the resistivity slightly decreased to ~ 138  $\mu\Omega$  cm from ~ 118  $\mu\Omega$  cm, while it significantly decreased to ~ 58  $\mu\Omega$ cm when the precursor pulsing time increased to 10 s. Figure 6 (b) showed the corresponding XRD analysis results. In the case of the film deposited with the precursor pulsing time of 1 s,

only three major peaks from the tetragonal RuO<sub>2</sub> were shown and one could not find the specific peaks from the HCP-Ru. However, when the precursor pulsing time increased to 5 s, a new peak from the HCP-Ru at ~  $44^{\circ}$  [Ru (101)] was developed, while the peak intensity from the RuO<sub>2</sub> increased as well. When the precursor pulsing time further increased to 10 s, the intensity of the XRD peak from the HCP-Ru (at  $2I = ~ 44^{\circ}$ ) significantly increased as compared to those of the film deposited with the precursor pulsing time of 5 s and the several peaks from the HCP-Ru were newly developed. These results indicated that the change in the resistivity of the film shown in Fig 6 (a) was mainly due to the change in the phase of the films with the precursor pulsing time.

Figure 7 (a) showed the resistivities of the films as a function of the deposition temperature. Here, the precursor and reactant pulsing times were set as 5 s and 60 s, respectively. The resistivity decreased continuously with increasing the deposition temperature and the resistivity of the film deposited at 270 °C was as low as ~ 35  $\mu$ Ω-cm. Figure 7 (b) showed the corresponding XRD analysis results. The film deposited at 185 °C only showed the peaks from the tetragonal RuO<sub>2</sub> phase and the peaks from the HCP-Ru were not detected. Meanwhile the film deposited at 225 °C showed the tiny peaks related to the HCP-Ru at 2I = ~ 44°. The peaks from the RuO<sub>2</sub> became broader and weaker with decreasing the deposition temperature from 225 °C to 185 °C, indicating the degradation of crystallinity and the decrease in the grain size. This could partly explain the increase in the resistivity at the given deposition temperature change. Interestingly, the film deposited at 270 °C showed that the lower deposition temperature is more favorable for the formation of the RuO<sub>2</sub> phase.

Most ALD processes of noble metals, including Ru, employ molecular oxygen as a reactant, the same as in this study. Interestingly, the results discussed above clearly addressed that a pure ALD-Ru as well as ALD-RuO<sub>2</sub> film could be controllably grown by adjusting the several process parameters such as the reactant gas flow ratio, reactant pulsing time, precursor pulsing time, and deposition temperature. Moreover, the oxygen content in the film could be widely tunable by controlling those parameters as well. In the Ru ALD, oxygen molecules were known to be dissociatively chemisorbed on the Ru metal surface as an atomic oxygen, and some oxygen atoms diffused into the subsurface region according to Aaltonen et al's [28] comprehensive work. The primary role of oxygen molecules is to oxidatively decompose the ligands of the adsorbed Ru precursor for the ALD Ru process. During the oxygen exposure step, the remaining ligands of the adsorbed Ru precursor react with incoming oxygen gas and, as a result, H<sub>2</sub>O, CO<sub>2</sub> as well a metallic Ru film are produced. When the amount of oxygen as compared to the Ru precursor is large enough, the equilibrium oxygen pressure in the deposition chamber might become high enough to form the large number of subsurface oxygen atoms. Under this condition, all of the subsurface oxygen atoms may not be consumed for the decomposition of Ru precursor ligands. Instead, these excessive oxygen atoms might form Ru-O bonds during the following Ru precursor exposure step, and result in both the incorporation of oxygen into the Ru and the formation of ruthenium oxide rather than the formation of metallic Ru. This situation could happen in this study, for instance, when we increased the oxygen flow rate and reactant pulsing time at the reactant pulsing step and decreased the precursor pulsing time. Moreover, it seems that each process happening during the Ru precursor pulsing and O<sub>2</sub> pulsing requires a certain energy barrier to proceed and the energy barrier for the formation of RuO<sub>2</sub> can be affected by the growth temperature. Above the certain temperature, the reaction between the adsorbed oxygen

atoms and the metal precursor seems to be so fast that all oxygen becomes consumed and metallic film is formed instead of an oxide, which is the case occurring at the deposition temperature at  $270 \,^{\circ}$ C.

### B. Growth kinetics and the properties of ALD-ruthenium oxide films

From above results, the pulsing conditions for  $RuO_2$  deposition were set to; the precursor pulsing time of 5 s, the reactant (200 SCCM O<sub>2</sub>) pulsing time of 60 s, and the purging time of 10 s. The deposition temperature was set to 225 °C because the higher-quality  $RuO_2$  could be deposited at 225 °C than at lower temperature (185 °C). Figure 8 showed the thicknesses of ALD-RuO<sub>2</sub> films deposited on the SiO<sub>2</sub> as a function of the number of ALD reaction cycles. Under the given pulsing conditions, the number of reaction cycles was varied from 50 to 200 cycles. The thickness was determined using XRR. The film thickness depended linearly on the number of ALD reaction cycles. From Fig. 8, the growth rate, which could be determined by linear extrapolation, was 0.19 nm/cycle and this is approximately 2 times higher than that of ALD-Ru. The extrapolated line showed that very small number of incubation cycles of ~ 2 was needed for the growth of ALD-RuO<sub>2</sub> films, proving high adsorption coverage of the precursors and a high reactivity of precursors with the reactant. Such aspects would lead to the fast nucleation of RuO<sub>2</sub> films on the SiO<sub>2</sub> surfaces.

To evaluate the nucleation behavior occurring at the initial stage of growth, the plan-view TEM analysis was performed on the samples deposited for the small numbers of cycles. Figure 9

showed the plan-view TEM images of RuO<sub>2</sub> films deposited on the thermally grown SiO<sub>2</sub> substrate as a function of the number of ALD reaction cycles. After only 3 cycles [Fig. 9 (a)], nuclei were clearly visible with the high density of  $2.19 \times 10^{12}$ /cm<sup>2</sup>. After 10 cycles, the nuclei density slightly decreased to  $1.81 \times 10^{12}$ /cm<sup>2</sup> with the start of the coalescence of nuclei [Fig. 9 (b)]. For further growth (30 cycles) [Fig. 9 (c)], the aggregation and coalescence occurred on the most of area and it seemed that almost continuous film was formed. Finally, the continuous and dense RuO<sub>2</sub> film was formed only with 40 cycles [Fig. 9 (d)] and the nominal thickness of that corresponds to ~ 6.5 nm in Fig. 8. From both Fig. 8 and Fig. 9, it should be emphasized that the nucleation of ALD-RuO<sub>2</sub> film was greatly enhanced as well as the growth rate of ALD-RuO<sub>2</sub> process was much higher than those of the ALD-RuO<sub>2</sub> processes using higher valence Ru precursors [18, 21, 24, 25], the same as the results of ALD-Ru using the same zero-valent Ru precursor [32]. For example, Kim et al.[18] reported that the growth rate of ALD-RuO<sub>2</sub> film deposited by modified ALD using Ru(II)(EtCp)<sub>2</sub> was 0.15 nm/cycle with 35 cycles of incubation period. Salaun et al.[21] reported that the growth rate of ALD-RuO<sub>2</sub> film using the same precursor was very low as 0.02 nm/cycle and the film was not continuous on the SiO<sub>2</sub> even after 700 ALD cycles. Results with another Ru(II) precursor, (methylcyclopentadienyl)(Pyrrolyl) Ru (MeCpPyRu) [24] showed the growth rate of ALD-RuO<sub>2</sub> was as low as 0.07 nm/cycle though the incubation cycle was not reported.

The film properties of ALD-RuO<sub>2</sub> film deposited with the optimized conditions ( $T_{dep}$ : 225 °C, gas ratio: 100 %, 5s-10s-60s-10s, for 200 ALD cycles) were briefly reported as follows. First, the film was analyzed by XRR (not shown here). XRR is known to be a nondestructive method of simultaneously determining a film thickness roughness, and density. In XRR, the film density can be estimated from the critical angle above which the X-rays start to penetrate into the film.

From the simulation, the density of  $RuO_2$  film was determined to 6.85 g/cm<sup>3</sup> which is only slightly lower than that of a bulk (6.97 g/cm<sup>3</sup>). The roughness and thickness of the film were determined to 0.33 nm and 32 nm, respectively. Considering the surface roughnesses of the ALD-RuO<sub>2</sub> films (10~20 nm in thickness) deposited with other precursors have been reported as approximately 1~3 nm, which is almost one-order higher than this study [21-23]. Therefore, it is obvious that the current process can provide an extremely smoother ALD-RuO<sub>2</sub> film, which might be probably due to the faster nucleation of the films.

Figure 10 showed the plan-view TEM analysis results of the ALD-RuO<sub>2</sub> film deposited with the optimized conditions. The bright-field (BF) TEM image of the film [Fig. 10 (a)] showed densely packed polycrystalline grains. The grain boundaries were not even clearly observable, supporting the quite high film density in the XRR analysis. The dark-field (DF) TEM image [Fig. 10 (b)] obtained by selecting the first order ring of the selected area diffraction pattern [Fig. 10 (c)] showed the crystalline grains with the size of ~ 15 nm. The corresponding SAD pattern of the film showed that the film formed the tetragonal structured  $RuO_2$  as corresponding to the XRD results.

Figure 11 showed the step coverage of the ALD-RuO<sub>2</sub> onto trenches with a very narrow top opening size of 25 nm and a high AR of 4.5. The step coverage of ALD-RuO<sub>2</sub> was very excellent, approximately ~ 100 %. This excellent step coverage indicated that the RuO<sub>2</sub> film was deposited under the ideal ALD growth conditions without partial decomposition of the precursors.

#### C. Thermal stability of ALD-ruthenium oxide films

In order to fabricate desirable device structures, films deposited during previous steps inevitably undergo thermal budget depending on post process conditions. Therefore, thermal stability of the deposited films must be evaluated under various ambients and temperatures. In this study, we investigated the thermal stability of ALD-RuO<sub>2</sub> thin films deposited with the optimized condition after annealing them in the ambient of N<sub>2</sub>, O<sub>2</sub> (10 SCCM in both cases), and N<sub>2</sub> + H<sub>2</sub> (45 and 5 SCCM, respectively) using a rapid thermal annealing (RTA) process.

Figure 12 showed the XRD patterns of the as-deposited and annealed samples under various annealing conditions. The diffraction peaks of the as-deposited film match to the crystal of tetragonal RuO<sub>2</sub> phase as shown in Fig. 2 (b). Even after RTA at 700 °C for 2 min under N<sub>2</sub> ambient, it seemed that the film kept the RuO<sub>2</sub> phase. A careful investigation on the XRD result showed that the peaks intensities from the HCP-Ru slightly increased while those from the RuO<sub>2</sub> slightly decreased as compared to those of the as-deposited film, indicating that the film started to transform into the metallic Ru. Even though, it should be noted that the most of  $RuO_2$  phases was still remained in the film even after annealing at 700 °C under N<sub>2</sub> ambient, indicating that the film was stable up to such a high temperature. In the case of the sample annealed under  $O_2$ ambient at 700 °C, the intensities of XRD peaks from the RuO<sub>2</sub> increased and the HCP-Ru phase Ru was not appeared. In contrast, at an RTA temperature of 500 °C under N<sub>2</sub>/H<sub>2</sub> ambient, the RuO<sub>2</sub> phase was fully reduced into Ru, indicating that H<sub>2</sub> gas effectively reduced the oxide films to the pure metal. It was reported that the ALD-RuO<sub>2</sub> film deposited with  $Ru(II)(EtCp)_2$ precursor and O<sub>2</sub> at 265 °C was reduced to Ru after annealing at NH<sub>3</sub> ambient at 500 °C [22]. In the case of  $RuO_2$  film deposited by modified ALD, it was also reported that the film was reduced

to Ru film after  $NH_3$  post-annealing. Thus, it could be thought that the  $H_2$  and  $NH_3$  ambient annealing can facilitate the reduction of  $RuO_2$  into the metallic Ru.

Figure 13 showed the corresponding plan-view SEM images of the as-deposited and the annealed ALD-RuO<sub>2</sub> films at various conditions. Only little changes in a grain size and a morphology were observable in the case of N<sub>2</sub> [Fig. 13 (b)] and O<sub>2</sub> ambient [Fig. 13 (c)] annealing at 700 °C as compared to that of the as-deposited sample [Fig. 13 (a)]. It also indicated that the film was stable even after such a high temperature annealing, which is the same results with the XRD analysis in Fig. 12. However, the plan-view SEM image of the sample annealed in N<sub>2</sub>/H<sub>2</sub> atmosphere at 500 °C showed a slight increase in the grain size and, at some location, the film was cracked [Fig. 13 (d)]. This phenomenon appeared to be related to the phase transformation of RuO<sub>2</sub> into Ru accompanying the release of oxygen in the film and the subsequent volume contraction.

#### D. Application of ALD-ruthenium oxide films as a bottom electrode of a MIM capacitor

Finally, the ALD-RuO<sub>2</sub> films deposited with the optimized conditions were evaluated as a bottom electrode of a MIM capacitor with high-*k* dielectrics. For the fabrication of MIM capacitor, an ALD-TiO<sub>2</sub> film with a thickness of 10 nm was deposited using tetrakis-dimethyl-amino-titanium (TDMAT) and O<sub>2</sub> plasma as a reactant on top of the ALD-RuO<sub>2</sub> bottom electrode with a thickness of 30 nm. The top electrode was also Ru (60 nm in thickness), which was deposited by sputtering using a shadow mask. Figure 14 (a) showed the C-V curve for this

MIM capacitor. One could see that the capacitors were well insulating and measurable, showing typical parameters of a high-*k* MIM capacitor. The capacitance was around  $6\mu$ F/cm<sup>2</sup> with a dielectric constant as high as ~68, indicating the formation of a rutile-structured TiO<sub>2</sub> film on the ALD-RuO<sub>2</sub> bottom electrode. This corresponded to an equivalent oxide thickness of 5.77 Å [EOT =  $t_{phy} \times (k_{SiO2}/k_{TiO2})$ ], where  $t_{phy}$ ,  $k_{TiO2}$  and  $k_{SiO2}$  are the physical thickness of TiO<sub>2</sub> and the dielectric constants of TiO<sub>2</sub> and SiO<sub>2</sub>, respectively. Figure 14 (b) showed the cross-sectional view high resolution TEM image of the ALD-TiO<sub>2</sub> grown on the ALD-RuO<sub>2</sub> bottom electrode. From the HRTEM image, the crystalline planes were clearly observed, whose lattice fringe spacing was very close to that of the rutile structured TiO<sub>2</sub>. The fast Fourier transformation of the HRTEM image [the inset of Fig. 14(b)] also indicated the formation of crystalline grains consisted of the rutile structure. The formation of rutile structured TiO<sub>2</sub> on the ALD-RuO<sub>2</sub> may explain the high dielectric constant of the MIM capacitor shown in Fig. 14 (a).

### IV. Summary and conclusions

In this study, the conductive and highly conformal ALD-RuO<sub>2</sub> thin films were grown on the thermally-grown SiO<sub>2</sub> substrates by ALD by using a sequential supply of the zero valent Ru precursor, EBCHDRu, and O<sub>2</sub> molecules. The results clearly showed that the pure ALD-Ru as well as the ALD-RuO<sub>2</sub> film could be controllably grown by adjusting the several process parameters, such as the reactant gas flow ratio, the reactant and precursor pulsing times, and the deposition temperature. The various thin film analysis results such as XRD, resistivity measurement, XPS, RBS, SIMS, and XRR showed that the formation of RuO<sub>2</sub> phase became

favorable with increasing both oxygen partial flow rate and pulsing time and with decreasing precursor pulsing time and the deposition temperature. From the rigorous selection of the deposition parameter, a tetragonal structured RuO<sub>2</sub> film (32-nm-thick) deposited at 225 °C was evaluated to have the resistivity of 118  $\mu\Omega$ -cm, the density of 6.85 g/cm<sup>3</sup> the grain size of ~ 15 nm, and the extremely smooth surface (0.33 nm of RMS roughness). It should be emphasized that the step coverage was perfect (~100 %) onto the extremely narrow trenches (top-opening width: 25 nm and AR: ~ 4.5) as well as the growth rate of ALD-RuO<sub>2</sub> was as high as 0.186 nm/cycle on the SiO<sub>2</sub> substrate with negligible incubation cycles. The ALD-RuO<sub>2</sub> film was thermally stable up to annealing at 700 °C in O<sub>2</sub> and N<sub>2</sub> ambient. The MIM capacitor consisted of sputtered-Ru/ALD-TiO<sub>2</sub>/ALD-RuO<sub>2</sub> showed the excellent performance with the dielectric constant of ALD-TiO<sub>2</sub> as high as ~ 68. This was definitely due to the formation of the rutilestructured TiO<sub>2</sub> film on top of the ALD-RuO<sub>2</sub> developed in this study, as evidenced by the HRTEM analysis.



Figure 1. Resistivity and (b) GIAXRD results of the films deposited on the SiO<sub>2</sub> substrate for 200 ALD cycles at the temperature of 225 °C as a function of the ratio of reactant flow rates  $[O_2/(O_2+N_2)]$ .



**Figure 2**. (a) Resistivity and (b) GIAXRD results of the films deposited on the SiO<sub>2</sub> substrates for 200 ALD cycles at the temperature of 225 °C as a function of reactant pulsing time. Here, the gas ratio of  $O_2/(O_2+N_2)$  was 100% (200 SCCM  $O_2$  without  $N_2$ ).



**Figure 3**. XPS Ru *3d* spectrum of the films deposited with various reactant pulsing condition. (a) 1 s, gas flow ratio of 20 %, (b) 1 s, (c) 10 s, (d) 30 s, and (f) 60 s. [The gas ratio was 100 % from (b) to (f)].



**Figure 4.** XPS O *1s* spectrum of the films deposited with various reactant pulsing times(a) 1 s, gas flow ratio of 20 %, (b) 1 s, (c) 10 s, (d) 30 s, and (f) 60 s. [The gas ratio was 100 % from (b) to (f)].



**Figure 5.** (a) RBS spectra of the film deposited on the  $SiO_2$  substrate with the reactant pulsing time of 60 s and (b) the ratio of O and Ru (O/Ru) in the films as a function of the reactant pulsing time. In (b), O/Ru ratio was calculated based on the SIMS depth profile results.



**Figure 6.** (a) Resistivities and (b) GIAXRD results of the films deposited on the thermally grown SiO<sub>2</sub> substrates for 200 ALD cycles at 225 °C as a function of the precursor pulsing time. The deposition conditions are as follows;  $O_2/(O_2+N_2)$  ratio of 100%, reactant pulsing time of 60 s, respectively.



**Figure 7.** (a) Resistivities and (b) GIAXRD results of the films deposited the on thermally grown SiO<sub>2</sub> substrates for 200 ALD cycles as a function of the deposition temperature. The deposition conditions are as follows;  $O_2/(O_2+N_2)$  ratio of 100%, precursor pulsing time of 5 s, and reactant pulsing time of 60 s.



**Figure 8.** Thicknesses of the RuO<sub>2</sub> films deposited on the thermally grown SiO<sub>2</sub> as a function of the number of ALD reaction cycles. The optimized conditions of the precursor pulsing time of 5 s, the reactant (200 SCCM O<sub>2</sub>) pulsing time of 60 s, the purging time of 10 s, and the deposition temperature of 225 °C were used. The line indicates the linear extrapolation of the thickness data.



**Figure 9.** Plan-view TEM images of the  $RuO_2$  films deposited on the thermally grown SiO<sub>2</sub> with the optimized conditions for (a) 3, (b) 10, (c) 30, (d) 40 ALD reaction cycles. The scale bar indicates 40 nm.



**Figure 10.** Plan-view TEM of the  $RuO_2$  films deposited on the thermally grown SiO<sub>2</sub> with the optimized conditions; (a) bright-field (BF) image, (b) dark-field (DF) image, and (c) selected-area diffraction pattern (SADP). The scale bar in (a) and (b) indicates 50 nm.



**Figure 11.** Cross-sectional view TEM image of showing the step coverage of the ALD-RuO<sub>2</sub> films onto the trench structures with the high AR of 4.5 (top opening width of the trench: ~ 25 nm). The scale bar indicates 25 nm.



Figure 12. GIAXRD results of the  $RuO_2$  films deposited on the thermally grown SiO<sub>2</sub> with the optimized conditions applied under various annealing conditions.



Figure 13. Plan-view SEM images of the  $RuO_2$  films with the optimized conditions applied under various annealing conditions; (a) as-deposited, (b) annealed in  $N_2$  ambient at 700 °C, (c) annealed in  $O_2$  ambient at 700 °C, and (d) annealed in  $N_2/H_2$  ambient at 500 °C. The scale bar indicates 250 nm.



**Figure 14.** (a) C-V curve of the MIM capacitor consisted of the ALD-RuO<sub>2</sub> bottom electrode and the ALD-TiO<sub>2</sub> high-*k* dielectric. (b) Cross-sectional view HRTEM image of the ALD-TiO<sub>2</sub> dielectric grown on the ALD-RuO<sub>2</sub> bottom electrode. Inset figure shows the fast Fourier transformation image of the crystalline TiO<sub>2</sub> grains. The scale bar in (b) indicates 2 nm.

#### **Corresponding Author**

\*Telephone: +82-53-810-2472. Fax: +82-53-810-4628.

E-mail: soohyun@ynu.ac.kr.

#### Notes

The authors declare no competing financial interest.

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1. Highly conformal and conductive  $RuO_2$  thin films were deposited without nucleation delay using a novel zero-valent Ru precursor by atomic layer deposition (ALD).

2. Effects of deposition conditions on the formation of RuO<sub>2</sub> phase were elucidated.

3. The performance as a bottom electrode of a metal-insulator-metal capacitor was evaluated.

4. The formation of a rutile-structured  $TiO_2$  film on top of the ALD-RuO<sub>2</sub> bottom electrode was demonstrated.

atomic layer deposition; ruthenium oxide; metallorganic precursor; nucleation; bottom electrode; capacitor