

## The properties of Ru films deposited by remote plasma atomic layer deposition on Ar plasma-treated SiO<sub>2</sub>

## Taeyong Park, Dongjin Choi, Hagyoung Choi, and Hyeongtag Jeon\*

Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea

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\* Corresponding author: e-mail hjeon@hanyang.ac.kr, Phone: +82 2 2220 0387, Fax: +82 2 2292 3523

By using remote plasma atomic layer deposition (ALD), ruthenium thin films were deposited on SiO<sub>2</sub> using bis(ethylcyclopentadienyl)ruthenium [Ru(EtCp)<sub>2</sub>] as a Ru precursor and an ammonia plasma as a reactant. Different plasma treatments were applied, and the best results were obtained with the Ar plasma-treated SiO<sub>2</sub> surface. The initial transition region usually observed with Ru deposition before continuous film formation was present, and the number of ALD cycles required to obtain a continuous film was reduced to about 35 cycles on the Ar plasma-treated SiO<sub>2</sub> substrates. The transition region of Ru cluster growth on Ar plasma-treated SiO<sub>2</sub> was investigated with transmission electron microscopy (TEM). Most of the Ru clusters were larger and better crystallized on the Ar plasmatreated SiO<sub>2</sub> than on untreated SiO<sub>2</sub>. Also, Ru films deposited on the treated SiO<sub>2</sub> exhibited a (002) preferred orientated structure with a film resistivity of about 10.26  $\mu$ Ω-cm. The growth rates of Ru after passing the transition region were similar on both the treated and untreated SiO<sub>2</sub> at about 1.7 Å/cycles. From the Auger electron spectroscopy (AES) spectrum, a very low content of oxygen was observed in the Ru films. About 9% carbon was detected by a rutherford backscattering spectrometer (RBS).

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1 Introduction In the past several decades, many transition metals had been employed in various parts of electronic devices. Typical uses of these metals are in gate and capacitor electrodes, and interconnect, diffusion barrier, and adhesion layers [1–4]. Ruthenium (Ru), a novel metal, has recently been extensively studied because it exhibits a high work function (4.5–5.3 eV) and low resistivity [5,6]. Ru is a candidate for application as a next generation metalinsulator-metal (MIM) capacitor electrode [7], which uses an ultra high-k material such a barium-strontium titanium oxide (BST) as Ru has good compatibility with BST [8, 9]. Generally, high work function metal electrodes enable an increased conduction band offset between the electrode and BST [10, 11]. The conduction band offset is an electron barrier, and a large band offset prevents leakage current between the top and bottom electrodes. The Ru (002) plane is also well aligned with the BST (110) plane. The dielectric constants of BST films deposited on (002) preferred oriented Ru films increased [6]. It is also expected that the loss of conductivity and electrical inhomogeneity in the MIM junction with high-k oxide are negligible, because Ru oxide

is a conducting material ( $\sim 46 \ \mu\Omega \ cm$ ) and also a high work function material [12, 13]. Ru thin films have been studied as adhesion layers or seed layers for Cu electrochemical plating (ECP) in a metallization process because of its good adhesion properties and immiscibility with Cu [14–16]. Ru exhibits good processability in contrast to other novel metals, because Ru can be etched easily by oxygen plasma or ozone gas [5]. However, ruthenium has some limitations for applications in mass produced systems such as the long transition time required to form a continuous film [17, 18] and its high material cost.

There are two main methods of Ru film deposition. One is thermal atomic layer deposition (ALD) with oxygen gas, and the other is plasma enhanced ALD with NH<sub>3</sub> plasma. Simply, the major difference between these two methods is the presence of plasma. For both methods, it is important to reduce the initial transient region before the continuous film deposition. It has been reported that NH<sub>3</sub> plasma pretreatment enhances the nucleation rate of Ru on a SiO<sub>2</sub> substrate with thermal ALD [18]. In the present study, several plasma pre-treatments were carried out on SiO<sub>2</sub> substrates and Ru films were deposited by remote plasma atomic layer deposition (RPALD). The characteristics of the films deposited on Ar plasma pre-treated  $SiO_2$  exhibited the best results among the several plasma treated substrates.

**2 Experimental** Ru thin films were deposited by RPALD using diethylruthenocene (98.9%, Ru(EtCp)<sub>2</sub>) as a Ru precursor and NH<sub>3</sub> plasma as a reactant. Ar gas was used both as a carrier gas and as a purge gas. All the gases flowed through a gas purifier to trap oxygen and moisture. Si substrates with thermally grown 100 nm thick SiO<sub>2</sub> layers were used. In order to compare the plasma effects, the Ru films were deposited on SiO<sub>2</sub> substrates that were plasma treated with argon, hydrogen, oxygen, and ammonia at 400 °C, and a SiO<sub>2</sub> substrate without plasma treatment. A downstream-type RPALD reactor with a 13.56 MHz radio frequency (rf) power source was used in this study. In order to prepare the plasma-treated SiO<sub>2</sub> substrates, 400 W of remote plasma was irradiated for 2 min in each gas environment. The substrate and canister containing  $Ru(EtCp)_2$  precursor were heated at 400 and 80 °C, respectively. The ALD process consists of the following four steps. First, Ar carrier gas was flowed at 50 sccm (standard cubic centimeter per minute) for 5 s for each cycle. Second, excess precursor was purged by flowing 80 sccm Ar gas for 10 s. Next, 100 W of NH<sub>3</sub> plasma was irradiated for 15 s. Finally, the remaining gas and by-products were also purged by flowing 80 sccm of Ar gas for 10 s. The plasma was an inductively coupled plasma type (ICP) and was generated at a distance of 15 cm from the substrate to the bottom of plasma region. The film thickness was measured by X-ray reflectivity. The film resistivity was calculated by a four point probe (FPP) using the thickness data. A transmission electron microscopy (TEM) was used to observe cross-sectional images of 40 nm thick Ru films on SiO<sub>2</sub> substrates. X-ray diffraction (XRD) was also used to investigate the crystal structures of the deposited Ru films.

**3** Results and discussion Figure 1 shows the growth rates of Ru films deposited on various plasma-treated SiO<sub>2</sub> substrates. Film thickness was measured by AES depth profiles with XRR calibration. A continuous Ru film was formed on the Ar plasma-treated SiO<sub>2</sub> substrate at about 30 ALD cycles, and the films on the other plasma-treated  $SiO_2$ substrates were formed at around 65 cycles. In thermal ALD, the NH<sub>3</sub> plasma pre-treatment affected the nucleation rate of Ru films [18]. However, in the RPALD process, there was no change of nucleation rate due to the NH<sub>3</sub> plasma pretreatment because the substrate was exposed to NH<sub>3</sub> plasma during each reaction step of the ALD cycles, not during pretreatment. After the continuous Ru film formed, the same linear growth rate of about 1.7 A/cycle was achieved. In the plasma treatment, we expect both chemical and physical effects. The chemical effects are the results of chemical reactions between the plasma and substrate, and the physical effects involve physical disorder of the SiO<sub>2</sub> surface such as



Figure 1 (online color at: www.pss-a.com) Evolution of thickness as a function of the number of cycles of Ru films deposited on plasmatreated and untreated  $SiO_2$  substrates.

physical etching or changes of the surface bonding state. However, for Ar plasma treatment, the chemical effects were negligible because Ar is an inert gas. The change of surface roughness by Ar plasma treatment was also negligible as the difference of the root mean square (rms) roughness measured by atomic force microscopy (AFM) was under 0.2 Å.

Figure 2 exhibits the impurities of the Ru films obtained by the AES depth profiles and differentiated AES spectra. Figures 2(a) and (b) show the AES depth profiles of the Ru films deposited for 150 cycles on the Ar plasma-treated and untreated SiO<sub>2</sub> substrates, respectively. The profiles of the impurities in the Ru films did not change with increasing film depth. Figures 2(c) and (d) show differentiated AES spectra which indicate that there are very low contents of oxygen and nitrogen impurities in the Ru films. Carbon detection is not available with AES because carbon KLL exactly matches the ruthenium MNN. Therefore, we utilized Rutherford backscattering spectrometer (RBS) measurements in order to measure the carbon contents of the Ru films. About 9.8 at% of carbon was detected in the 50 nm thick Ru film by RBS, as shown in Fig. 3. The impurity levels could also be estimated from the film resistivity. The film resistivities of Ru deposited on Ar plasma-treated and untreated SiO<sub>2</sub> were 10.26 and 15.25  $\mu\Omega$  cm, respectively. These values are slightly higher than the bulk resistivity of about 7  $\mu\Omega$  cm due to carbon contamination and a thickness effect. The impurity levels of Ru films deposited on the treated and untreated SiO<sub>2</sub> were almost the same but the film resistivity varied. The grain sizes of the Ru films on the Ar plasma-treated and untreated SiO<sub>2</sub> substrate were probably different.

Figure 4(a) and (b) shows plane view TEM images of Ru clusters on Ar plasma-treated and untreated SiO<sub>2</sub> after 20 and 30 ALD cycles, respectively. Ru clusters were larger on the Ar plasma-treated SiO<sub>2</sub> than the clusters on the untreated SiO<sub>2</sub> surface. The number densities of Ru clusters on the treated and untreated SiO<sub>2</sub> were about  $3.33 \times 10^{-11}$  and  $6.28 \times 10^{-11}$  cm, respectively. As shown in the crosssectional TEM images in Fig. 4(c) and (d), the Ru films deposited on the Ar plasma-treated SiO<sub>2</sub> consisted of larger







**Figure 2** (online color at: www.pss-a.com) AES depth profiles of Ru films deposited for 150 cycles on (a) Ar plasma-treated and (b) untreated SiO<sub>2</sub> substrates. And differentiated AES spectra of (c) nitrogen and (d) oxygen.

grains than the films deposited on the untreated  $SiO_2$  substrate. The different number densities of the Ru clusters may have caused the grain size differences in the thick continuous Ru films. In addition, the Ru grains grew vertically and finally formed columnar structured films. Therefore, the orientations of the Ru films should be measured by XRD.



**Figure 3** (online color at: www.pss-a.com) RBS data for a 50 nm thick Ru film deposited on an untreated  $SiO_2$  substrate.



**Figure 4** TEM plane view images of Ru clusters deposited for (a) 20 cycles on Ar plasma-treated  $SiO_2$  and (b) 30 cycles on untreated  $SiO_2$ . Cross-sectional view images of about 40 nm thick Ru films deposited on (c) Ar plasma-treated  $SiO_2$  and (d) untreated  $SiO_2$ . The scale bars in the images are 20 nm for plane view images and 50 nm for cross-sectional view images.

Figure 5 shows XRD patterns of hexagonal close-packed (HCP) Ru films deposited for 50, 150, and 300 ALD cycles on Ar plasma-treated and untreated SiO<sub>2</sub> substrates. The samples were measured in the  $2\theta$  range of 25–60°. In Fig. 5, the (002) peak ( $2\theta = 44.1^{\circ}$ ) of the Ru film deposited on the Ar plasma-treated SiO<sub>2</sub> was about six times higher than that on untreated SiO<sub>2</sub> in the diffraction patterns of the films subjected to 150 cycles. The intensity ratios of the major peaks of fully randomly oriented Ru films are shown at the bottom of Fig. 5 along with a bar graph for reference. XRD data indicate that the *c*-axis (002) preferred orientation



**Figure 5** (online color at: www.pss-a.com) XRD patterns of Ru films deposited on Ar plasma-treated and untreated SiO<sub>2</sub>. The samples were measured in the  $2\theta$  range from  $25^{\circ}$  to  $60^{\circ}$ . The (002) peaks were observed at 44.1°.

occurred significantly on the Ar plasma-treated  $SiO_2$  substrate. Figure 4(a) also shows that the clusters on the Ar plasma-treated  $SiO_2$  were formed with a hexagonal shape. Generally, additional Ru adatoms could be attached easily on a loosely-packed plane because the plane is the most similar structure with gas phase. Then Ru clusters with a loosely packed (100) plane which is parallel to the surface, become larger. As a result, the Ru clusters which faced a non-(002) direction grew slower than those that faced the (002) direction. Then, the small clusters finally disappeared by coalescence.

The preferred orientation frequently occurred on SiO<sub>2</sub>. In the growth of clusters, the maximum density of clusters is controlled by the capturing area if there is no cluster coalescence. The ideal capturing area is a circular area inside of a radius of the surface diffusion length of an additional adatom. In the capturing area, the adatoms are easily attached to existing clusters through surface diffusion rather than staying on fixed bonded sites. The surface diffusivity is mainly related to the deposition temperature. In addition, the capturing radius of a nucleus increases with increasing temperature. However, the true mobility of Ru adatoms is affected not only by surface diffusivity but also by the surface roughness and chemical state of traps (e.g., adsorption sites). When there are too many adsorption sites, growth is disturbed because the capturing areas overlap each other. Therefore, the number densities of adsorption sites affect the capturing area. The SiO<sub>2</sub> surface is normally covered with hydroxyls and the surface hydroxyls can be detached from SiO<sub>2</sub> surface by thermal annealing or Ar plasma treatment [19]. Therefore, the hydroxyl-removed SiO<sub>2</sub> surface after Ar plasma treatment contains many broken bonds and can easily form surface amine ligands under NH<sub>3</sub> plasma ambient during the deposition process. Transition metals bond strongly with oxygen on the surface, and the surface hydroxyl on  $SiO_2$  may therefore be a better adsorption site for oxidative reactions than the surface amine for reductive reactions of Ru deposition. Therefore, it the surface mobility of Ru adatoms may increase as the density of surface hydroxyls decreases after Ar plasma pretreatment. The surface with less adsorption sites (e.g., hydroxyls) also provides a large capturing area for clusters and the Ru films deposited on the Ar plasma-treated  $SiO_2$ have large grains and (002) preferred orientation.

Much Ru deposition research regarding CVD or ALD has focused on the initial growth of Ru, because it has a relatively long transition region. Among the several plasma pretreatments that were introduced in this paper, Ar plasma pre-treatment is possibly capable of changing the surface bonding state and improving growth rate and film properties.

**4 Conclusions** In the initial stages of deposition, the characteristics of deposited films were affected mainly by surface chemicals or physical states. Several plasma pretreatments were carried out, and among the treatments chosen in this study, the Ar plasma treatment of the  $SiO_2$  substrate yielded the best results to form continuous films. On the  $SiO_2$  substrate, relatively large clusters were formed

in the transition region and finally, large (002) preferred oriented grains were observed in the continuous film. By Ar plasma pre-treatment, some surface hydroxyls were replaced with amines. The presence of too many oxidative adsorption sites prevents lateral growth of Ru clusters by limiting the capturing area. Consequently, Ar plasma pre-treatment enhances adatom mobility by removing oxidative reaction sites which prevents lateral growth of Ru clusters and the (002) preferred orientated Ru film with large grains were deposited. The application of Ar plasma treatment before Ru deposition in the RPALD method, which used NH<sub>3</sub> plasma as a reactant, enabled a reduction of the process time and the formation of a well matched Ru film with other perovskite structured films such as BST and STO.

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