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Investigation on the Growth Initiation of Ru Thin Films by Atomic Layer Deposition

Seong Keun Kim, Jeong Hwan Han, Gun Hwan Kim, and Cheol Seong Hwang*

Department of Materials Science and Engineering and Inter-university Semiconductor Research Center, Seoul National University, Seoul 151-744, Korea

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Ru thin films were grown on Au, Pt, TiN, TiO_2, and SiO_2 substrates by atomic layer deposition using 2,4-(dimethylpentadienyl)(ethylcyclopentadienyl)Ru (DER) dissolved in ethylcyclohexane at a concentration of 0.2 M as the Ru precursor and O_2 as the reactant. There was a long incubation time for Ru film deposition on TiN and SiO_2 due to the weak interaction between DER and the covalent bonds in TiN and SiO_2. On the other hand, the Ru films on TiO_2 exhibited a shorter incubation time. There was a negligible incubation time for Ru film deposition on Au and Pt due to the strong interactions between the DER precursor and metallic surfaces, resulting in a smooth surface morphology and strong *c*-axis texture. A continuous Ru film, not an island-shaped film, was formed on Au, which does not catalytically dissociate molecular oxygen, even at a film thickness of 1 nm. Therefore, the initial growth of Ru thin films was determined by the adsorption of the metal precursor not the catalytic dissociation of molecular oxygen.

I. Introduction

Ru thin films have attracted considerable attention for applications as capacitor electrodes in dynamic random access memory (DRAM)[1−4] and as a diffusion barrier in the Cu metallization process[5−7] owing to its high work function, low resistivity, and ease for etching. In particular, it was reported that the dielectric constants of TiO_2 and Al-doped TiO_2 films were increased significantly on Ru electrodes when the films were grown by atomic layer deposition (ALD) using oxidants with a strong oxidation potential, such as O_3 and plasma-activated O_2 or N_2O, due to the structural compatibility between rutile TiO_2 and in situ formed RuO_2 at the interface.[8−11] In addition, the applications of Ru thin films have recently been extended beyond microelectronics to nanoscience.[12−19] The formation of Ru nanoparticles, nanotubes, and nanowires using the thin film processes was reported.[12−18] The preparation of Ru/aerogel nanocomposites via an ALD process was also reported.[19]

ALD is the most promising deposition method to the formation of conformal Ru films on the three-dimensional hole structures in DRAM devices as well as on complex structures for nanomaterials on account of its unique self-limiting mechanism. There are many reports on ALD growth of Ru thin films, and most ALD processes for the growth of Ru thin films use oxygen as a reactant.[20−25]

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*To whom correspondence should be addressed. E-mail: cheolsh@snu.ac.kr.

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It was reported that molecular oxygen is adsorbed dissociatively on a Ru surface, which has catalytic activity for oxygen dissociation, and some of the atomic oxygen diffuses into the subsurface region.[20] During the subsequent injection of a metal precursor, the metal precursor consumes the adsorbed oxygen atoms by a reaction between the ligands of the metal precursor and adsorbed oxygen atoms, producing a Ru metallic film.[20] However, this reaction mechanism represents the growth behavior of Ru films during the steady-state stage of growth, where a Ru layer is grown on a predeposited Ru layer, and cannot be applied to the initial growth stage on heterogeneous substrates. This is because the adsorption of the Ru metal precursor is dependent on the substrate, and heterogeneous substrates usually have different catalytic activity for oxygen dissociation than for the Ru layer.

In the initial ALD growth stage, the nucleation of a deposited material is strongly dependent on the properties of the substrate surface, where the chemical reaction occurs. The difference in nucleation in the initial growth stage can affect the properties of the film bulk. Therefore, understanding the initial growth behavior of Ru films in ALD is crucial for applications that require very thin Ru films. In some cases, very long incubation cycles for nucleation were reported, which is quite detrimental to the formation of nanometer thickness scale uniform films.[21,26]

However, there have been few systematic studies on the initial growth of Ru thin films by ALD, and there is no report on the effect of the catalytic activity for oxygen dissociation on the initial growth stage. Therefore, Ru thin films were grown by ALD on various substrates using O_2 as the reactant to understand the initial growth of Ru films in this study. Pt film substrates were used because both Pt and Ru are noble metals and Pt can dissociate O_2 and the Ru precursor owing to its catalytic activity.[27-29] The initial growth behavior of Ru on Pt might represent the steady-state growth of a thicker Ru film (on Ru itself). Other substrates, Au, TiN, TiO_2, and SiO_2, with different catalytic activity and bonding characteristics were also used. The initial growth behavior and surface morphology of the films was examined carefully depending on the types of the substrate. The results showed that the adsorption of the Ru precursor rather than the dissociative adsorption of molecular oxygen is the governing step for growth initiation of Ru films.

II. Experimental Procedure

Ru thin films were grown by ALD using a shower head-type reactor (Quros Co., Plus-200). The ALD system was equipped with a pulse liquid injector and a thermal vaporizer to evaporate the Ru solution. 2,4-(Dimethylpentadienyl)(ethylcyclopentadienyl)Ru (DER, from Tosoh Co.) dissolved in ethylcyclohexane (ECH) at a concentration of 0.2 M was used as the Ru source. The Ru solution was injected into the vaporizer for 6 ms and flash-evaporated. The vapor was then transported to the reactor by Ar carrier gas at a flow rate of 50 sccm. O_2 at a flow rate of 1000 sccm was used as the reactant. The reactor was purged with Ar gas at a flow rate of 1000 sccm. The Ru thin films were deposited at growth temperatures of 250 and 290 °C. ALD TiO_2, sputtered TiN, thermal SiO_2, sputtered Pt, and e-beam evaporated Au films were used as substrates to understand the growth behavior of Ru thin films at the initial stage on different substrates. The detailed deposition conditions are reported elsewhere.[30]

The areal density of Ru ions in the growing films was measured by X-ray fluorescence spectroscopy (XRF, Themoscientific, ARL Quant'X). The film thickness and density of the Ru films was evaluated by X-ray reflectivity (XRR), and the surface morphology of the Ru films was investigated by atomic force microscopy (AFM, JEOL, JSPM-5200). The crystalline structure and preferred orientation of the Ru films was examined by $\theta - 2\theta$ X-ray diffraction (XRD, PANalytical, X'pert Pro). The chemical binding states of the Ru films were determined by X-ray photoelectron spectroscopy (XPS, ThermoVG, SIGMA PROBE). The impurity concentration, including oxygen, in the films was examined by Auger electron spectroscopy (AES).

III. Results and Discussion

The initial growth of the films by ALD shows different features from that of steady-state growth because the properties of the reaction surface change as the depositing material is adsorbed on the surface during the initial growth stage. Depending on the properties of the substrate, the growth rate at the initial growth stage can be enhanced or decreased compared to the growth rate at the steady state. In order to approach the steady-state growth rate, a certain number of cycles, which are known as the "incubation cycles" in an ALD process, are required. In particular, ALD processes for the growth of noble metal films, such as Ru, Ir, and Pt, usually require a larger number of incubation cycles and are more dependent on the type of substrate compared to the ALD processes for the growth of oxide and nitride films.[21,31] Therefore, this study examined the growth behavior of Ru thin films on a range of substrates by ALD. Figure 1a shows the change in the areal density of Ru ions in the Ru films as a function of the number of cycles when the films were grown at a growth temperature of 250 °C. The areal density of Ru atoms on the Pt and Au substrates increased linearly with an increasing number of cycles over the entire range, and the incubation cycles for the growth of the Ru films was negligible on these two substrates. On the other hand, the growth of the films on the TiN and TiO_2 substrates was retarded at the initial growth stage. After a certain number of cycles (approximately 100 and 200 cycles on

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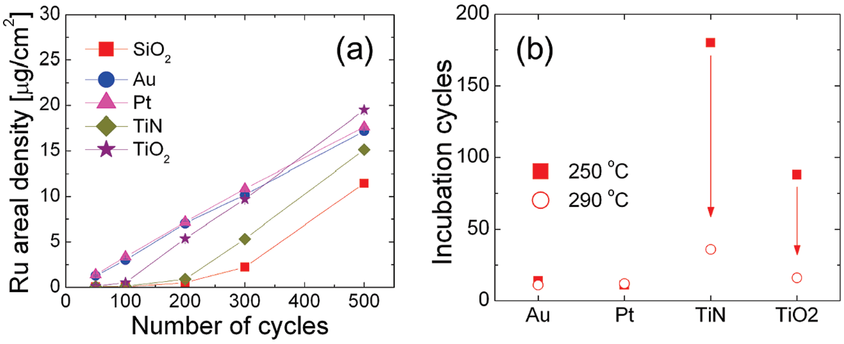

Figure 1. (a) Areal density of Ru ions in the films on various substrates as a function of the number of cycles. (b) Incubation cycles for the growth of Ru films on Au, Pt, TiN, and TiO_2 (films were grown at 250 and 290 °C, respectively).

the TiO_2 and TiN), the growth rate of the films recovered from delayed growth. The Ru films on SiO_2 substrates showed a large number of incubation cycles. Moreover, the steady-state growth of Ru films on SiO_2 substrates was not confirmed, even up to 500 deposition cycles. The steady-state growth rate (35 ng/cm^2·cycle) of Ru films on Pt and Au substrates was slightly lower than that (47 ng/cm^2·cycle) on TiN and TiO_2. This difference in steady-state growth rate might be due to the different crystallographic orientation of Ru films, as shown below.

The incubation cycles were examined at two different growth temperatures, 250 and 290 °C, to determine the influence of growth temperature on the initial growth behavior of Ru films. Figure 1b shows the number of incubation cycles on the Au, Pt, TiN, and TiO_2 substrates. The Ru films on Au and Pt substrates showed a small number of incubation cycles (~10 cycles) irrespective of the growth temperature. Considering the error range, the Ru films on Au and Pt substrates might have formed in a steady-state growth pattern even at the first growth stage with negligible incubation time for nucleation. The number of incubation cycles of the Ru films on TiN substrates was 180 at 250 °C, which is larger than the 90 observed on TiO_2 substrates at the same temperature. However, the number of incubation cycles of Ru films on TiN and TiO_2 substrates was decreased significantly (to 40 and 20 cycles on TiN and TiO_2, respectively) at a growth temperature of 290 °C. This suggests that the nucleation behavior of Ru films on TiN and TiO_2 substrates is a thermally activated process. On the other hand, the nucleation of Ru on Au and Pt substrates was not affected by the thermal energy. The steady-state growth rate of Ru on Au and Pt at 290 °C was almost identical to that of 250 °C while that on TiN, TiO_2, and SiO_2 at the same temperature was slightly higher. This suggests that 290 °C belonged to the ALD temperature regime.

As the formation of nuclei on a substrate is difficult during the ALD process where a large number of incubation cycles are observed, most of the injected precursors are adsorbed on preformed nuclei rather than on the substrate itself. This might result in island-type growth and the formation of large grains, which eventually produces a rough surface morphology. Therefore, the relationship between the surface morphology of the Ru films and substrates was examined by considering the different number of incubation cycles on the different substrates. Figure 2 shows AFM images of the Ru films on (a) Au, (b) Pt, (c) TiN, (d) TiO_2, and (e) SiO_2 substrates when the Ru films were grown at a growth temperature of 250 °C by 500 cycles. The Ru film thicknesses on Au, Pt, TiN, and TiO_2 substrates were 14−17 nm but only approximately 10 nm on SiO_2. The Ru films on Au substrates contained small grains (< 20 nm), whereas those on TiN and TiO_2 substrates contained relatively large grains (20−30 nm). On the SiO_2 substrate, where the number of incubation cycles was highest, the Ru film had larger grains (30−50 nm). The large grain sizes of 60−100 nm observed in the lower panel of Figure 2b might originate from the large grains of the Pt substrate, not from the Ru film itself. To show clearly this aspect, an AFM image of Pt substrate was included in upper left panel of Figure 2b. The upper right panel of Figure 2b shows the AFM image of Ru film on Pt substrate with the identical vertical scale to the other AFM images to compare the roughness. For a further understanding of the surface morphology of the films, the variation in the root-mean-square (rms) roughness of the Ru films on a range of substrates was examined (Figure 2f). The rms roughness values of the substrates were also included in Figure 2f because the surface morphology of Ru films was affected by the type of substrate in the ALD process. The Ru films on Au and Pt substrates, which showed a negligible incubation cycle, exhibited a negligible difference in the rms roughness between Ru films and substrates. However, the Ru films on TiN, TiO_2, and SiO_2, which showed a long incubation cycle, exhibited a substantial difference in the rms roughness. This result supports that the long incubation cycle induces a rough surface morphology due to difficult formation of nuclei. In particular, a rms roughness value of the Ru film on the Pt substrate is very close to the value of the Pt substrate. It is supposed from this result that the large grains in Figure 2b correspond not to the Ru film but to the Pt substrate. The Ru film on the TiO_2 substrate also showed protrusions of 80−100 nm. Further study will be needed to understand the origin of these protrusions.

The thin Ru films on various substrates were examined by XPS. Figure 3a shows the Ru 3d XPS spectra of the Ru films grown on SiO_2, TiN, Pt, Au, and TiO_2 substrates. In order to examine more carefully the island-type growth

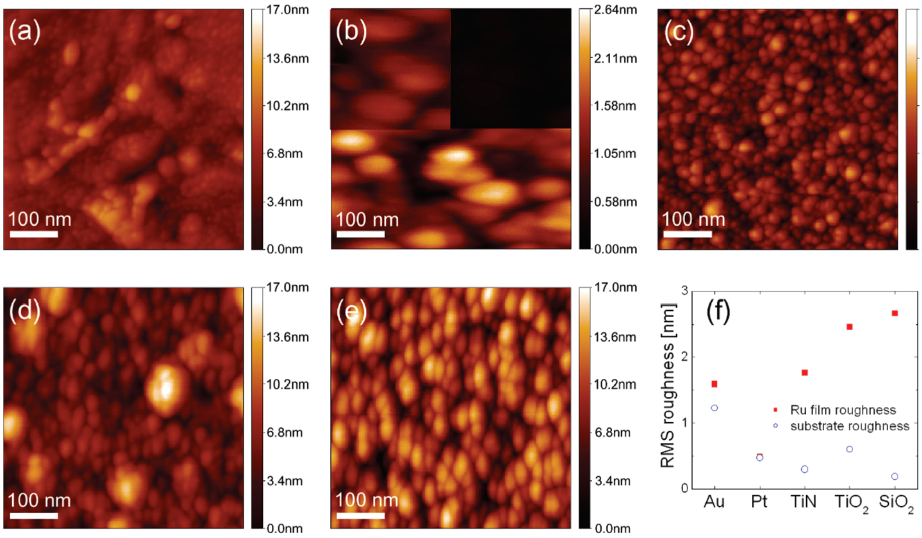

Figure 2. AFM images showing the surface morphology of the Ru films on (a) Au, (b) Pt, (c) TiN, (d) TiO_2, and (e) SiO_2. (f) Variation in the rms roughness of Ru films on various substrates and substrates..

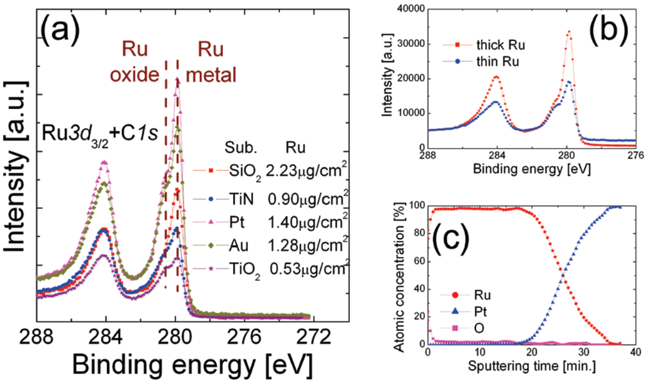

Figure 3. (a) Ru 3d XPS spectra of thin Ru films on Au, Pt, TiN, TiO_2, and SiO_2. Area density in the figure was measured by XRF. (b) Ru 3d XPS spectra of the thick and thin Ru films on Pt substrate. (c) AES depth profile of 15 nm-thick Ru film on Pt substrate.

behavior of Ru films on various substrates, very thin Ru films (< 3 nm) were chosen for the XPS measurement. The number of deposition cycles was 300 for the Ru film on SiO_2, 200 for the Ru film on TiN, 50 for the Ru film on Pt, 50 for the Ru film on Au, and 100 for the Ru film on TiO_2. Although it was attempted to compare the Ru films with the same Ru areal density, there were some deviations due to the different incubation time of Ru film growth with respect to the substrates. XRF data represent the total amount of Ru deposited as its information depth is much larger than the Ru film thickness while XPS data represent only a very thin surface region of Ru film. Therefore, the smaller XPS intensity of Ru film on SiO_2 substrate compared to that from Ru on Pt or Au substrate, despite the higher XRF intensity, suggests the island-type growth behavior of Ru film on this substrate at the initial growth stage. The areal densities of Ru atoms in the films were as low as 0.5−2.2 (±0.1) $\mu g/cm^2$, which correspond to a thickness of 0.4−2 nm. Interestingly, the Ru 3d peak of the Ru films on Au and Pt substrates had a higher intensity than that of the Ru film on the SiO_2 substrate despite XRF indicating a smaller areal density of Ru atoms. XRF is a bulk-sensitive technique while XPS is a surface sensitive technique. This seemingly contradictory result strongly suggests that the Ru grew in a more island-like manner on SiO_2 than on Au and Pt substrates. Island-like nucleation leaves relatively large uncovered substrate surface area by the Ru nuclei resulting in the lower XPS intensity. This result is consistent with the long incubation cycle and rough morphology of the Ru films on SiO_2 in Figures 1 and 2e, respectively. The intensity of the Ru 3d XPS spectra of the Ru films on TiN and TiO_2 substrates compared to the relative XRF intensity also suggests island-type growth behavior on these substrates, even though it is less obvious.

The Ru 3d XPS spectra in Figure 3a show a Ru $3d_{5/2}$ peak from both metallic Ru bonding and an oxide phase. The peak from the oxide phase might be due to Ru oxide, which was formed natively on the surface because the films were exposed to the air before XPS analysis. However, it is possible that oxygen at the interface may contribute to the XPS signal of the Ru oxide phase due to very thin film thickness. To further understand the origin of the oxide phase, 15 nm-thick Ru film on Pt substrate was also examined by XPS and the Ru 3d spectra of the thick Ru film was compared with the spectra of the thin Ru film. Figure 3b shows Ru 3d XPS spectra of the thick and thin Ru films on Pt substrate. The thick Ru film also showed the Ru $3d_{5/2}$ peaks corresponding to the oxide and metal phases like the thin Ru film. The intensity of the Ru $3d_{5/2}$ peak corresponding to the oxide phase in the XPS spectra of the thick Ru film is comparable to the intensity in the XPS spectra of the thin Ru film while the contribution from the metal phase in the thick Ru film is shown to be larger than that in the thin Ru film. The difference in the intensity of the peak from the metal phase is because the analysis depth of XPS for Ru is larger than the film thickness of the thin Ru film. To confirm further the absence of oxygen at the interface, the depth profile of the 15 nm-thick Ru film on Pt substrate

Table 1. Difference in Electronegativity of the Substrate Atoms

	difference in electronegativity
Ti−N	1.5
Ti−O	1.9
Si−O	1.54

was examined by AES. (Figure 3c) Oxygen piled up at the interface was not observed in Figure 3c. Therefore, it can be understood that the contribution from the oxide phase in Figure 3a mainly came from natively formed Ru oxide on the surface.

It was recently suggested that electron donation from conducting substrates to the adsorbed precursor molecules would enhance precursor decomposition and the removal of ligands from the precursor molecules for several ALD or chemical vapor deposition (CVD) processes using different metal, alloy, and compound materials.[32] However, in this study, the Ru films on the TiN substrate showed retarded growth behavior at the initial growth stage despite the electrically conducting properties of TiN. There were an even larger number of incubation cycles compared to the Ru films on the TiO_2 substrate, which had insulating properties. Therefore, the adsorption of the Ru precursor molecules and the nucleation of Ru films are not due to electron donation from the substrate.

The bonding nature of the substrate can affect the adsorption of precursor molecules. It was reported that the ionic character of the substrate enhanced the nucleation of films in the CVD process of metal films, such as Al and Ru.[33−35] Therefore, the bonding nature of the substrates was examined in terms of electronegativity. Table 1 shows the difference in electronegativity between the component atoms in the substrates.[36] The difference in electronegativity of TiO_2 is larger than that of TiN and SiO_2, suggesting that TiO_2 has more ionic character than TiN and SiO_2. It should be noted that the number of incubation cycles of the Ru films on TiO_2 was smaller than that on TiN and SiO_2, as shown in Figure 1. This supports the hypothesis that the ionic character of the substrate enhances the adsorption of Ru precursor molecules. However, the Ru films on TiN substrates had a smaller number of incubation cycles than the Ru films on SiO_2 substrates, even though the difference in electronegativity of TiN is comparable to that of SiO_2. There may be Ti−N and Ti−O bonds on the TiN surface because the surface of TiN exposed to air was partially oxidized. The coexistence of Ti−N and Ti−O bonds may reduce the incubation cycle of Ru films on TiN substrates.

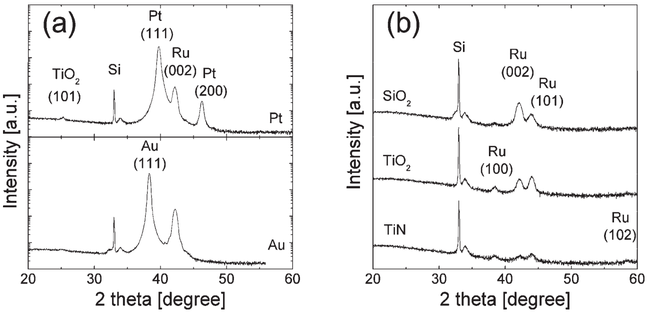

Figure 4. $\theta - 2\,\theta$ XRD patterns of the Ru films on (a) Au and Pt and (b) TiN, TiO_2, and SiO_2 substrates.

In addition, the growth of Ru films on metal Au and Pt substrates showed a negligible incubation cycle. Since the effect of electron donation on the nucleation of films is not considered to be the main controlling factor, the metallic bonding nature of the surface was assumed to enhance the adsorption of Ru precursor molecules. In ionic materials, electrons are transferred from the cations to anions, and the electrostatic force between them creates ionic bonding. In metals, the valence electrons are removed from each atom to form a communal electron sea, in which the positively charged ions are dispersed. Therefore, it is believed that the adsorption of Ru precursor molecules on ionic and metallic materials is enhanced by the interaction between the charged ions in the substrates and the precursors. However, such electrostatic interactions are not expected in covalent materials; hence, the growth of Ru films on them shows larger incubation cycles.

The crystalline structure of the Ru films on different substrates was examined by XRD. Figure 4 shows $\theta - 2\,\theta$ XRD patterns (log scale intensity in *y*-axis) of the Ru films on (a) Au and Pt and (b) TiN, TiO_2, and SiO_2 substrates, respectively. The Ru films on the Au and Pt substrates showed Ru grains with a highly *c*-axis preferred orientation as understood from the very high (002) peak intensity. No other peaks from Ru except for (002) were observed in Figure 4a. Although the position of the Au (111) peak overlaps somewhat with the position of the Ru (100) peak, it is believed that Ru grains on the Au substrate are highly *c*-axis preferred oriented because of well-matched crystal structures and lattice parameters between face-centered cubic structured Au (111) and hexagonal Ru (002) planes. On the other hand, the Ru films on TiN, TiO_2, and SiO_2 showed several diffraction peaks. On TiN, there were contributions from the (100), (002), (101), and (102) Ru planes, where the peak intensity was comparable to each other. The Ru film on TiO_2 was crystallized with several orientations of Ru (100), (001), and (101). The intensity of the (100) peak was weaker than that of the (002) and (101) peaks, and the intensity of the (002) peak was comparable to that of the (101) peak. (100), (002), and (101) peaks were also observed on SiO_2. However, the (100) peak made a lesser contribution, and the intensity of the (002) was higher than that on TiO_2. In addition, the Ru peaks on TiN, TiO_2 and SiO_2 showed a much weaker intensity than those on the Au and Pt

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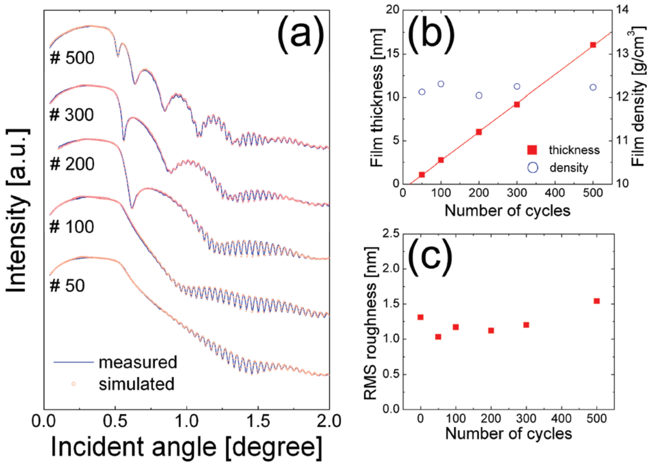

Figure 5. (a) XRR spectra of Ru films on Au substrates and (b) the thickness and density and (c) rms roughness of the Ru films on Au substrates as a function of the number of cycles.

substrates. Consequently, the Ru films on Au and Pt had a strong *c*-axis texture due to structural compatibility between Au and Pt (111) and Ru (002) planes, whereas the Ru films on TiN, TiO_2, and SiO_2 were grown with a somewhat random orientation due to island-type growth. This suggests that the bond characteristics of the substrate also affect the crystallographic orientation of the resulting Ru films.

The ALD processes of noble metal films, such as Ru, Ir, and Pt, commonly employ oxygen as a reactant.[20-25,30] In these processes, molecular oxygen is chemisorbed dissociatively on the reaction surface. The ligands of the subsequently injected metal precursor are decomposed by the reaction with the adsorbed oxygens. The dissociation of molecular oxygen depends on the catalytic properties of the noble metal. At the initial growth stage, when the substrate is not covered completely with the depositing material, molecular oxygen cannot be chemisorbed with dissociation on the substrate if it does not have catalytic properties. To further understand the effect of the catalytic properties on the initial growth of Ru films, the growth of the Ru films on Au substrates was examined in detail because Au does not catalytically dissociate molecular oxygen.[37,38]

Figure 5a shows the XRR spectra and simulated data of the Ru films on Au substrates. The number of cycles for the growth of Ru films on Au substrates was varied from 50 to 500. All the simulated data fitted the measured XRR spectra well. Figure 5b shows the evaluated thickness and density from XRR analysis of the Ru films on Au substrates as a function of the number of cycles. The film thickness increased linearly with increasing number of cycles. The growth rate calculated from the slope of the graph was 0.033 nm/cycle, and the number of incubation cycles was 18, which is comparable to the number of incubation cycles in Figure 1. The density of all the films was ~12.2 g/cm^3, which was ~98% of the bulk value (12.4 g/cm^3). The calculated density of the noncontinuous films such as island-shape films from XRR should be much lower than the value for bulk materials. However, the density of the Ru films was similar to that of bulk Ru irrespective of the film thickness down to ~1 nm. This suggests that the Ru films were grown on Au substrates without a delay in nucleation. In addition, the surface roughness of the Ru films on Au substrates was examined because an island structure should increase the surface roughness with increasing film thickness. Figure 5c shows the change in the rms roughness of the Ru films on the Au substrates as a function of the number of cycles. The rms roughness of the Au substrate is also shown in Figure 5c (number of cycles = 0). The rms roughness of the Ru films was almost constant up to 300 cycles and increased slightly at 500 cycles. Interestingly, the rms roughness of the Au substrate was reduced by the deposition of a ~1 nm-thick Ru film. This also shows that Ru films were grown on Au substrates without a delay in nucleation despite the absence of any catalytic effects for the dissociation of molecular oxygen.

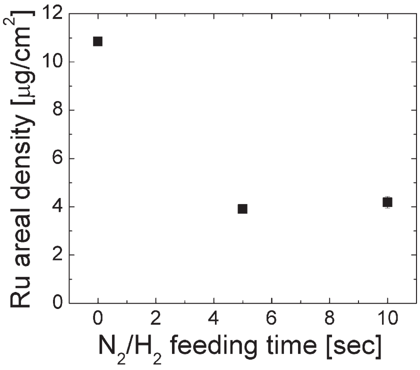

Figure 6. Variation in the areal density of Ru ions in the films on Pt substrate as a function of the feeding time of N_2/H_2..

These results show that at the initial growth stage the adsorption of metal precursor plays a decisive role in the growth of Ru films rather than the chemisorption of atomic oxygen from the dissociation of molecular oxygen. This means that the Ru precursor can be adsorbed easily on a metallic surface, even though the metallic surface is oxygen free. It was recently reported that Ir thin films were grown by ALD using a cycle consisting of $Ir(acac)_3$, ozone and H_2 pulses.[39] Although the pulse step of H_2 removed the oxygen adsorbed on the surface, the injected $Ir(acac)_3$ precursor was well chemisorbed on the reduced surface. This also shows that the presence of oxygen on the reaction surface barely affects the adsorption of the metal precursor.

To further clarify the fact that the adsorption of DER precursor, not dissociative adsorption of molecular oxygen, governed the growth initiation of Ru films, Ru films were grown on Pt substrates by ALD using a cycle consisting of DER, O_2, and 1000 sccm N_2/H_2(5%) steps like the sequence in ref 39. The consecutive feeding of N_2/H_2 in this sequence removes adsorbed oxygen immediately prior to the DER pulse. If the dissociative adsorption

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of molecular oxygen governs the growth initiation of the films, no film must be grown using this sequence. Figure 6 shows the variation in the areal density of Ru ions in the films as a function of the feeding time of N_2/H_2. All the films were grown for 300 cycles. It is obvious in Figure 6 that Ru films were still grown by ALD despite the consecutive H_2 step. The areal density of Ru ions in the film with a N_2/H_2 feeding time of 10 s is approximately identical to the areal density of the film with a N_2/H_2 feeding time of 5 s, suggesting that the consecutive N_2/H_2 feeding completely removed the adsorbed oxygen above a N_2/H_2 feeding time of 5 s. Although the film is thinner than the Ru film grown without feeding of H_2, the still achieved Ru growth is believed to be due to a different reaction route when oxygen is not present. If there are the adsorbed oxygen atoms on the reaction surface, the injected Ru precursor can be adsorbed on the surface by the reaction with the adsorbed oxygens as suggested in ref 20. Without the adsorbed oxygens on the surface, however, the injected Ru precursor can be adsorbed by the interaction of the precursor and substrate. The different reaction route leads to the difference in the Ru areal density in Figure 6. It is quite obvious that the adsorption of the Ru precursor, not the dissociative adsorption of molecular oxygen, determines the growth initiation of Ru films irrespective of the different reaction route.

IV. Conclusion

Ru thin films were grown on Au, Pt, TiN, TiO_2, and SiO_2 substrates by ALD with DER dissolved in ECH as the Ru precursor and O_2 as the reactant. On a covalent SiO_2 substrate, Ru film nucleation showed a long incubation delay, whereas the Ru films on the ionic (TiN(O) and TiO_2) and metallic (Au and Pt) surface exhibited shorter and almost no incubation cycle, respectively. The bond characteristics of the substrate play a decisive role in the adsorption of the metal precursor. Although Au and Pt have completely different catalytic properties for the dissociation of molecular oxygen, Ru thin films on both Au and Pt substrates showed a similar nucleation and growth behavior. Therefore, the initial growth of the Ru thin films is determined by the adsorption of the metal precursor rather than by the dissociative adsorption of molecular oxygen on the substrate or Ru film itself. Furthermore, it is believed that this conclusion can apply to the ALD process of several other noble metals such as Ru, Pt, Ir, and Rh which is based on the oxidative reaction mechanism. It needs to be reminded that the growth of bulk Ru film definitely requires oxygen supply.

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