

DOI: 10.1002/cvde.200906789

Full Paper

Atomic Layer Deposition of Ruthenium Thin Films from an Amidinate Precursor**

By Hongtao Wang, Roy G. Gordon,* Roger Alvis, and Robert M. Ulfig

Ruthenium thin films are deposited by atomic layer deposition (ALD) from bis(*N,N'*-di-*tert*-butylacetamidinato)ruthenium(II) dicarbonyl and O₂. Highly conductive, dense, and pure thin films can be deposited when oxygen exposure, E_O , approaches a certain threshold (E_{max}). When $E_O > E_{max}$ the film peels off due to the recombinative desorption of O₂ at the film/substrate interface. Analysis by atomic probe microscopy (APM) shows that the crystallites are nearly free from carbon impurity (<0.1 at.-%), while a low level of carbon (<0.5 at.-%) is segregated near the grain boundaries. APM also shows that a small amount of O impurity (0.3 at.-%) is distributed uniformly between the crystallites and the grain boundaries.

Keywords: ALD, O₂ exposure, Ruthenium thin films

1. Introduction

Smooth ruthenium thin films with low resistivity and high purity are candidates for various applications in microelectronics. Such applications include electrodes for both dynamic random access memories and metal-oxide-semiconductor field effect transistors,^[1] and seed layers for copper interconnections.^[2] Ru has a conductive oxide, RuO₂, which makes it an ideal substrate for oxide dielectrics deposited with ozone, such as rutile phase TiO₂.^[3] Ru thin films have been deposited by both physical vapor deposition (PVD) and CVD; however ALD is still preferred for conformal deposition for structures with very high aspect ratios.

Several ALD ruthenium precursors have been studied. The cyclopentadienyl (Cp) compounds, such as RuCp₂ and Ru(EtCp)₂,^[2,4,5] and the tris-β-diketonates (thd) compounds, such as Ru(thd)₃,^[6] have been studied with O₂ as co-reactant. The ruthenium amidinate precursor, bis(*N,N'*-

di-*tert*-butylacetamidinato)ruthenium(II) dicarbonyl, has been synthesized in our group and used to deposit ruthenium thin films with, or without, NH₃ as co-reactant.^[7,8] Highly pure and conductive films have been conformally deposited in holes with aspect ratios 40:1.^[8] In this research, we report an ALD process for ruthenium thin films using this amidinate precursor and O₂. We found that the growth mechanism is quite different from the process using NH₃ as a co-reactant.

2. Results and Discussion

The oxygen exposure has a significant effect on the growth behavior, structure, and properties of ALD Ru films. The O₂ exposure (E_O) can be estimated from the number of O₂ molecules dosed per ALD cycle (n_O), the pumping speed (S), and the deposition temperature (T_h), as shown in Equation 1.

$$E_O = \frac{n_O R T_h}{S} = \frac{P_O V_O T_h}{S T_O} \quad (1)$$

R is the ideal gas constant, P_O , V_O , and T_O the pressure, volume (5 mL), and temperature (413 K), respectively, of the O₂ trap. The pumping speed, S , is about 2.7 L · s⁻¹ for an Edwards vacuum pump, RV8, used in this ALD reactor. A first observation is that, for Ru films deposited at 325 °C (Fig. 1), the growth rate increases from ~0.3 Å per cycle to 1 Å per cycle after the introduction of O₂. This may be due to the enhanced surface reactivity of the dissociatively adsorbed oxygen on the surface and the region just below the surface. The growth rate is relatively constant for O₂ exposures from 0.015 Torr · s to 0.035 Torr · s. Similar

[*] Prof. R. G. Gordon
Department of Chemistry and Chemical Biology, Harvard University
Cambridge, MA 02138 (USA)
E-mail: gordon@chemistry.harvard.edu

Dr. H. Wang
School of Engineering and Applied Science, Harvard University
Cambridge, MA 02138 (USA)

R. Alvis
FEI Company
5350 NE Dawson Creek Drive, Hillsboro, Oregon 97124 (USA)

R. M. Ulfig
Imago Scientific Instruments
5500 Nobel Drive, Madison, WI 53711 (USA)

[**] This work was performed in part at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation under NSF award no. ECS-0335765. CNS is part of the Faculty of Arts and Sciences at Harvard University.

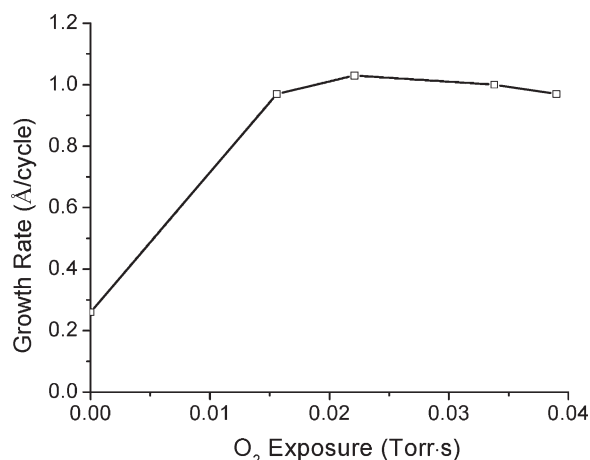


Fig. 1. The dependence of Ru thin film growth rate on the O₂ exposure at the deposition temperature of 325 °C.

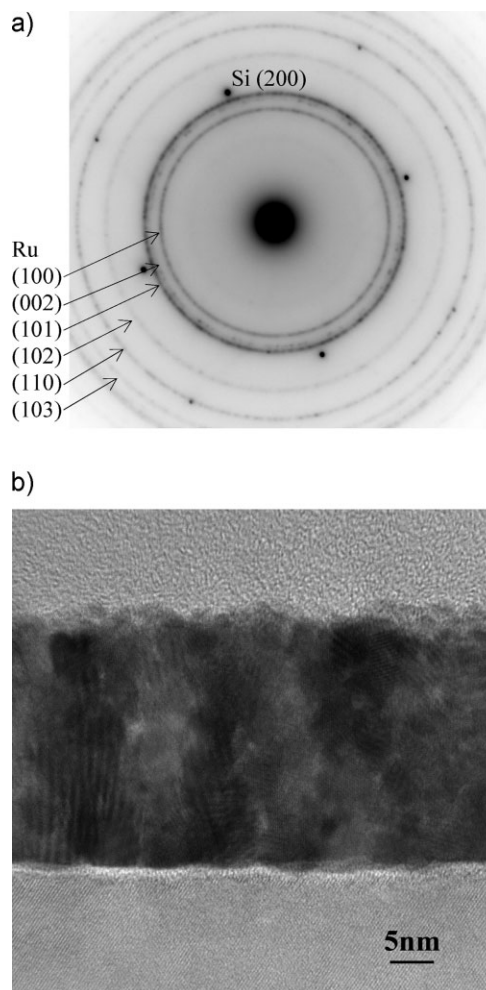


Fig. 2. a) ED and b) cross-sectional TEM image of Ru film/Si deposited at 325 °C with O₂ as co-reactant.

Table 1. Comparison of the lattice spacings of rutile RuO₂ (PCPDF File No. 88-0322), hexagonal Ru (PCPDF File No. 65-7645), and measurements from ED.

Rutile RuO ₂		Hexagonal Ru		ED
plane	<i>d</i> -spacing [Å]	plane	<i>d</i> -spacing [Å]	<i>d</i> -spacing [Å]
(110)	3.177	(100)	2.338	2.333
(101)	2.555	(002)	2.137	2.146
(200)	2.247	(101)	2.051	2.052
(111)	2.221	(102)	1.577	1.566
(210)	2.009	(110)	1.350	1.345
(211)	1.687	(103)	1.216	1.219

behaviors were also observed in ALD Ru film depositions from Ru(thd)₃,^[6] RuCp₂,^[4,5] and Ru(EtCp)₂.^[9]

Figure 2a shows the electron diffraction (ED) pattern with Si(200) diffraction spots as an internal scale. The calculated lattice spacing and the relative intensity closely match the hexagonal Ru phase (Table 1) from powder X-ray diffraction (XRD) (PCPDF File No. 65-7645). No rings from the RuO₂ phase have been observed by ED. Figure 2b shows the cross-sectional transmission electron microscopy (TEM) image of a typical Ru film deposited with O₂ at 325 °C. The Moiré fringes extend through the thickness indicating that the grain size is comparable to the film thickness. No stacking structure of RuO₂/Ru was observed.

X-ray photoelectron spectroscopy (XPS) spectra in Figure 3a show that the Ru film has a high oxygen concentration in the topmost layer. After 30 s Ar⁺ (3 keV) sputtering cleaning, the oxygen level decreases below the detection limit (~1%) of the XPS, which is consistent with the low solubility of oxygen in bulk Ru, and further proves there is no buried RuO₂ phase.^[10] The XPS spectra did not change after subsequent Ar⁺ sputtering for longer times. The high resolution XPS of O 1s (Fig. 3b) confirms the oxygen peak is comparable to the background noise. No N impurities have been detected. Due to the overlap between C 1s and Ru 3d_{3/2} peaks, XPS cannot measure the carbon content straightforwardly; however the low resistivity (~10 μΩ cm) and high density (~12.3 g cm⁻³) of a 30 nm ALD-produced Ru film imply that the carbon concentration is also low.

More sensitive detection of impurities was done with APM, which uses the time-of-flight (TOF) mass spectrometry (MS) and point-projection microscopy to identify, in 3D, where atoms were originally located in the specimen.^[11,12] A film stack, Co₄N (5 nm, capping layer)/Ru (10 nm, region of interest)/WN (3 nm, adhesion layer) (Fig. 4a), was deposited on a coupon with pre-sharpened Si micro-tips (tip radius ~10 nm, covered with a thin layer of thermal SiO₂) (Fig. 4b), which can be used directly as an APM sample without being contaminated by the standard sample preparation. A 10 nm Ru film was conformally deposited around the micro-tip, as is shown in the 3D Ru atom mapping (Fig. 5), in which each dot represents 7 Ru atoms. Figure 6 shows the elemental depth profiles across the Co₄N/Ru interface. The overlap region of Co and Ru is ~1.5 nm, which is same as the surface

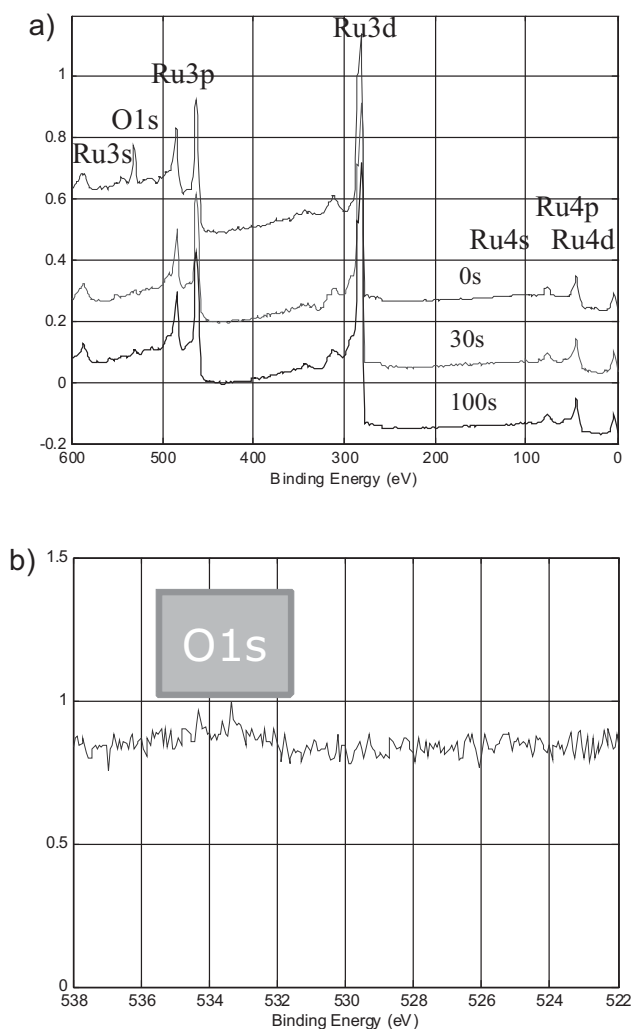


Fig. 3. a) XPS spectra (Al K α radiation, $h\nu = 1486.6$ eV) of a 30 nm Ru thin film with low energy (3 keV) Ar⁺ sputtering for 0 s, 30 s, and 100 s. b) High resolution XPS image of O 1s after 30 s Ar⁺ sputtering.

roughness. C is concentrated at the interface due to transferring the sample after Ru deposition to another reactor for Co₄N capping. The C tail decreases in the same fashion as Co, which suggests that the near-interface impurities come from the surface contamination. The N profile is ~ 1 nm deeper into the Ru film than Co, which is due to the N diffusion during Co₄N deposition with NH₃. A sample without Co₄N capping does not show any N content, which is consistent with XPS observations. The grain structure of the Ru film can be recognized by the greater atomic density in the grain interior compared to the grain boundary (GB) (Fig. 7a). The dashed lines in the Ru 2D map indicate the GB locations. Comparing the 2D map of C atoms (Fig. 7b) to the Ru map shows that the C atoms mostly segregate along the GBs. The local impurity concentration can be calculated by counting the different atom numbers inside a given region. In the GB region (box A), C and O concentrations are 0.48 at.-% and 0.27 at.-%, respectively, while inside the grain (box B), they are 0.08 at.-% and

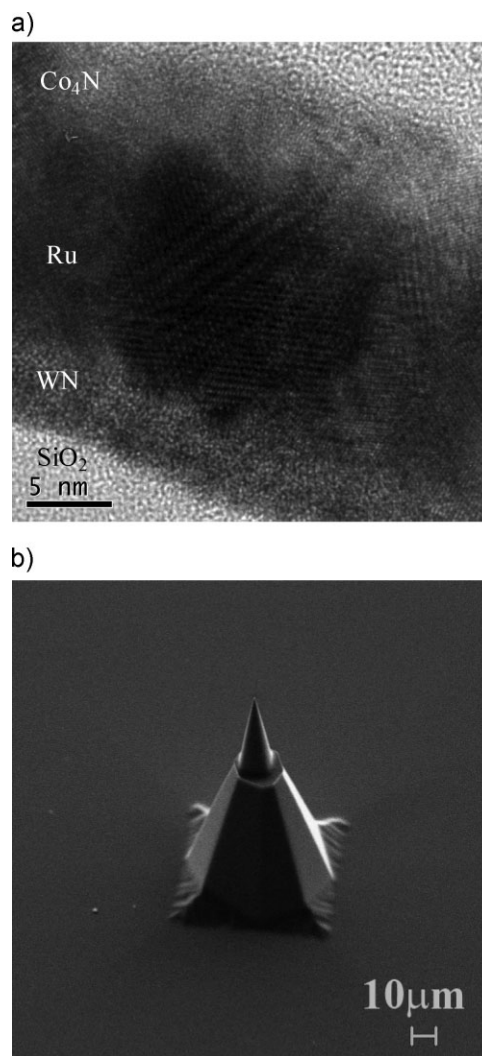


Fig. 4. a) Cross-sectional TEM image of the film stack on a planar SiO₂/Si substrate. b) SEM image of the pre-sharpened micro-tip.

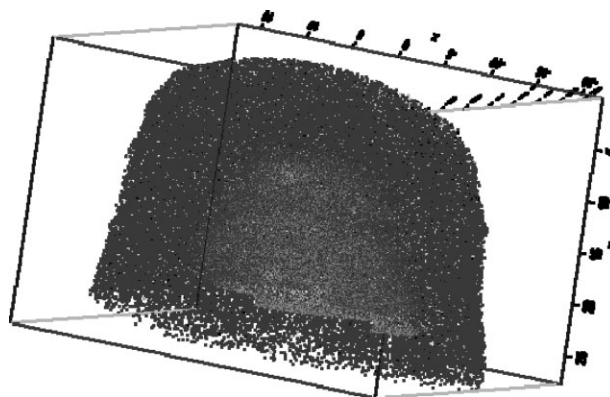


Fig. 5. The 3D mapping of Ru atoms.

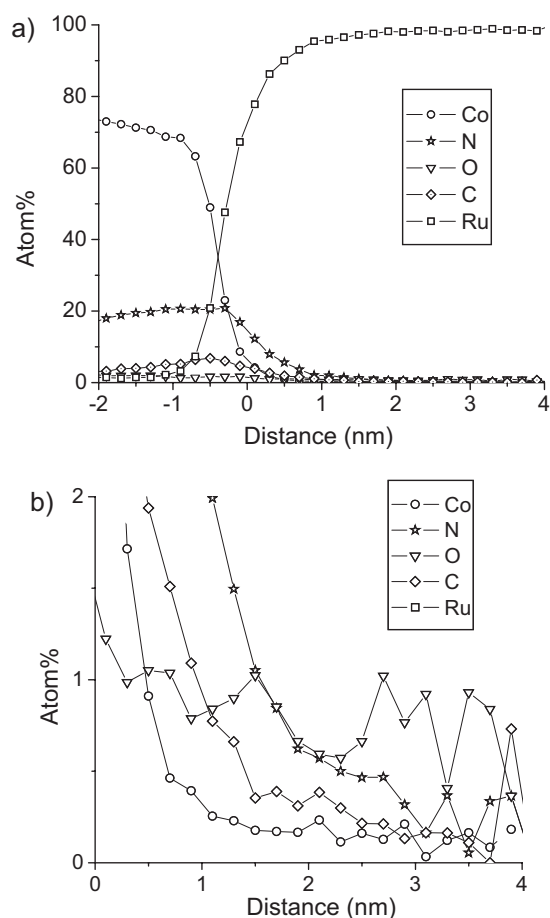


Fig. 6. a) The elemental depth profiles across the $\text{Co}_4\text{N}/\text{Ru}$ interface. b) The details of impurity distribution across the interface.

0.27 at.-% respectively. The C concentration decreases by a factor of 6 from the GB to the grain interior, while O concentration remains the same. The line profile across the grain boundary (Fig. 7c) clearly shows that the C atoms mostly distribute in a 5 nm wide region near the GB.

Ru crystals have a hexagonal, close-packed lattice with $c/a \approx \sqrt{8/3}$, which contains interstices of octahedral and tetrahedral types. The octahedral interstice has room for a spherical atom of 0.56 \AA radius, and the tetrahedral interstice for one of only 0.29 \AA . The octahedral interstice size is much smaller than the C atom radius (0.77 \AA), but close to the O atom radius (0.60 \AA). The atom size determines that C atoms are most likely to be accommodated in the GB regions, which have a more open structure, while O atoms can distribute inside the crystallites without causing significant distortion of the lattice. Regions with a high C impurity content thus have poor crystallinity and low density, as observed along the GBs in our experiments. The average impurity concentration for C and O are $0.30 \pm 0.05 \text{ at.-%}$ and $0.27 \pm 0.03 \text{ at.-%}$, respectively, for an interior slab of Ru film not including atoms located in the surface or interface regions. The grains are $\sim 20 \text{ nm}$ in size on the micro-tip and comparable to films deposited on planar substrates (Fig. 4a).

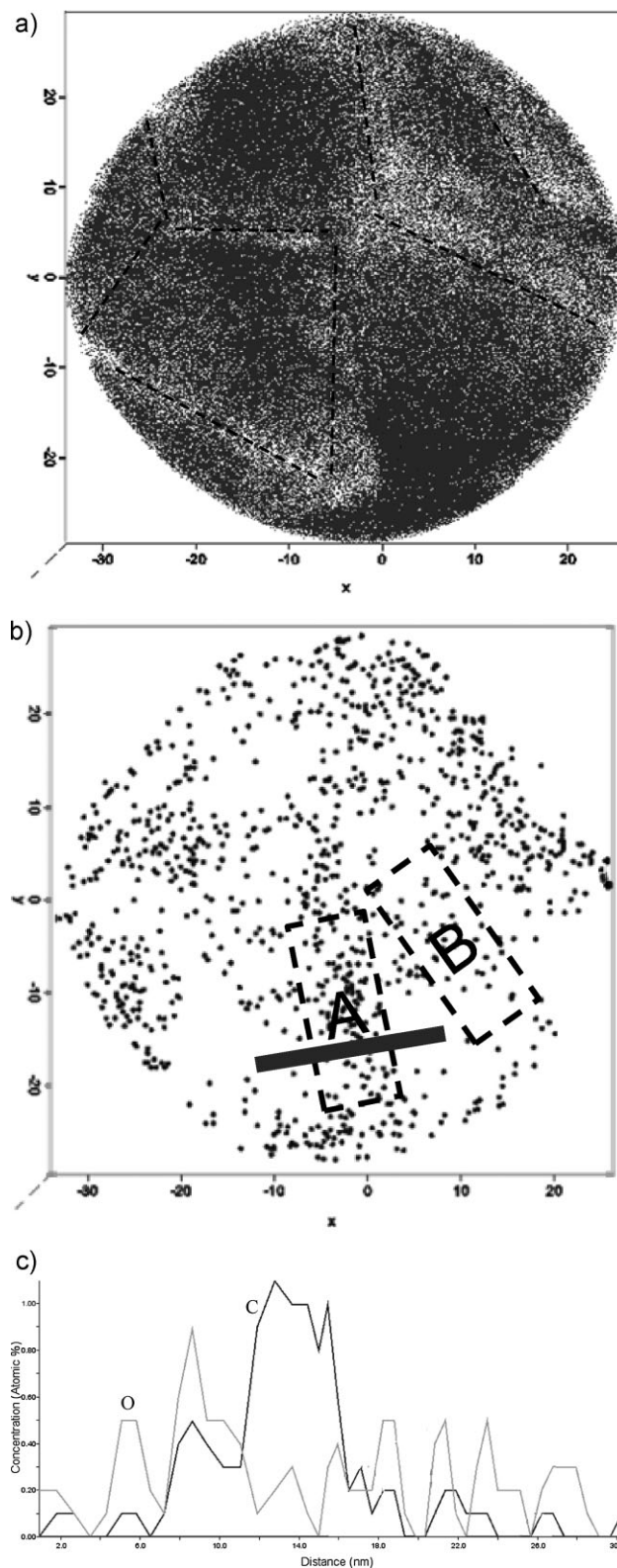


Fig. 7. The 2D atom mappings of a) Ru and b) in a slice 5 nm thick. In b), boxes A and B indicate the area for local impurity concentration calculation. The line in b) indicates the profiling location. c) The C and O line profile across the GB.

When the O_2 exposure is above $0.04 \text{ Torr} \cdot \text{s}$ at 325°C , the Ru films change abruptly from a specular silver look to a milky look with flakes observable to the eye. Scanning electron microscopy (SEM) images in Figure 8 show that these flakes were not from gas-phase reactions, but result from the film peeling off the substrate. Since Ru atoms are

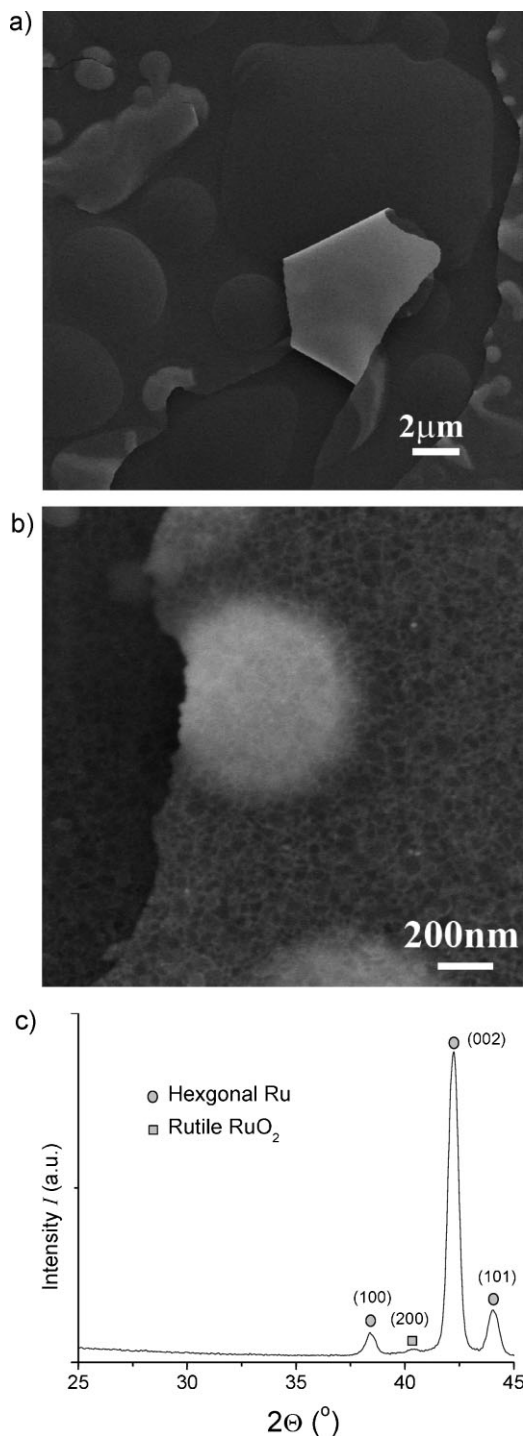


Fig. 8. a) low and b) high magnification SEM images and c) grazing angle XRD spectrum of Ru thin film deposited at 325°C and $E_{O_2} = 0.04 \text{ Torr} \cdot \text{s}$.

mobile under high O_2 exposure, the film stress will be reduced at higher O_2 exposure. Also the film has a thickness of only 15–30 nm, so the film stress has a negligible effect on the film peeling; therefore, the round bumps indicate that some gas species evolved near the film/substrate interface, causing the film to become detached. This is in contrast to the annealing behavior of Ru thin films in an O_2 gas atmosphere. No change in morphology was observed for Ru films annealed at 325°C and under 40 Torr in O_2 (5%) and N_2 mixture for 30 min (SEM images not shown). For annealing in O_2 at more elevated temperatures, instead of peeling the Ru film was seriously roughened by oxidation.^[9] The film peeling during deposition presents a paradox. Large amounts of oxygen can be accommodated in the Ru surface or subsurface region (e.g., equivalent of 20 to 30 monolayers for Ru(0001))^[13] while the solubility of oxygen in bulk Ru is exceedingly low.^[10] Denoting, C_O , C_R , and C_B as the concentrations of oxygen in subsurface layer after O_2 pulse and after Ru precursor vapor pulse, and the bulk solubility, respectively, we expect $C_O \gg C_R \sim C_B$ for a good deposition. Incomplete consumption of subsurface oxygen will lead to $C_O > C_R > C_B$ and formation of a super-saturated layer after many ALD cycles. The interstitial oxygen atom has a radius somewhat larger than the octahedral interstice and needs to deform the close-packed Ru atoms for accommodation. As the film grows thicker, the percent of the GB atoms is reduced and the chemical potential for interstitials is increased. The energy can be decreased by lowering the oxygen concentration in three possible ways; (1) diffusion of oxygen to the subsurface layer, (2) recombinative desorption of oxygen after diffusion to the film/substrate interface,^[14] and (3) formation of buried RuO_2 and escape by further oxidizing some of RuO_2 to RuO_x ($x = 3$ or 4).^[15,16] The round bumps imply that the desorption of O_2 or RuO_x are the most likely mechanisms.

To distinguish the mechanism (2) from (3), it is critical to see whether the fractured Ru film is strongly oxidized. The formation of crystalline RuO_2 was not observed for films deposited at various temperatures and oxygen exposures by XRD and electron diffractions. The reason may be that the lattice structures of RuO_2 (tetragonal) and Ru (hexagonal) are quite different. Energy is needed to form GBs between two phases, which increases the activation energy barrier for RuO_2 nucleation. The amorphous phase of RuO_2 can also be excluded because of the good crystallinity (30–50 nm grain size in Fig. 8b).^[17] Grazing angle XRD (Fig. 8c) shows that all the three main peaks come from the hexagonal Ru phase and only a very weak peak can possibly be assigned to rutile RuO_2 (200), which may be due to post-deposition oxidation of the surface by air exposure. The grain size (L) can also be estimated from the Stokes and Wilson method,^[18] using Equation 2.

$$L = \frac{\lambda}{\beta \cos \theta}, \quad (2)$$

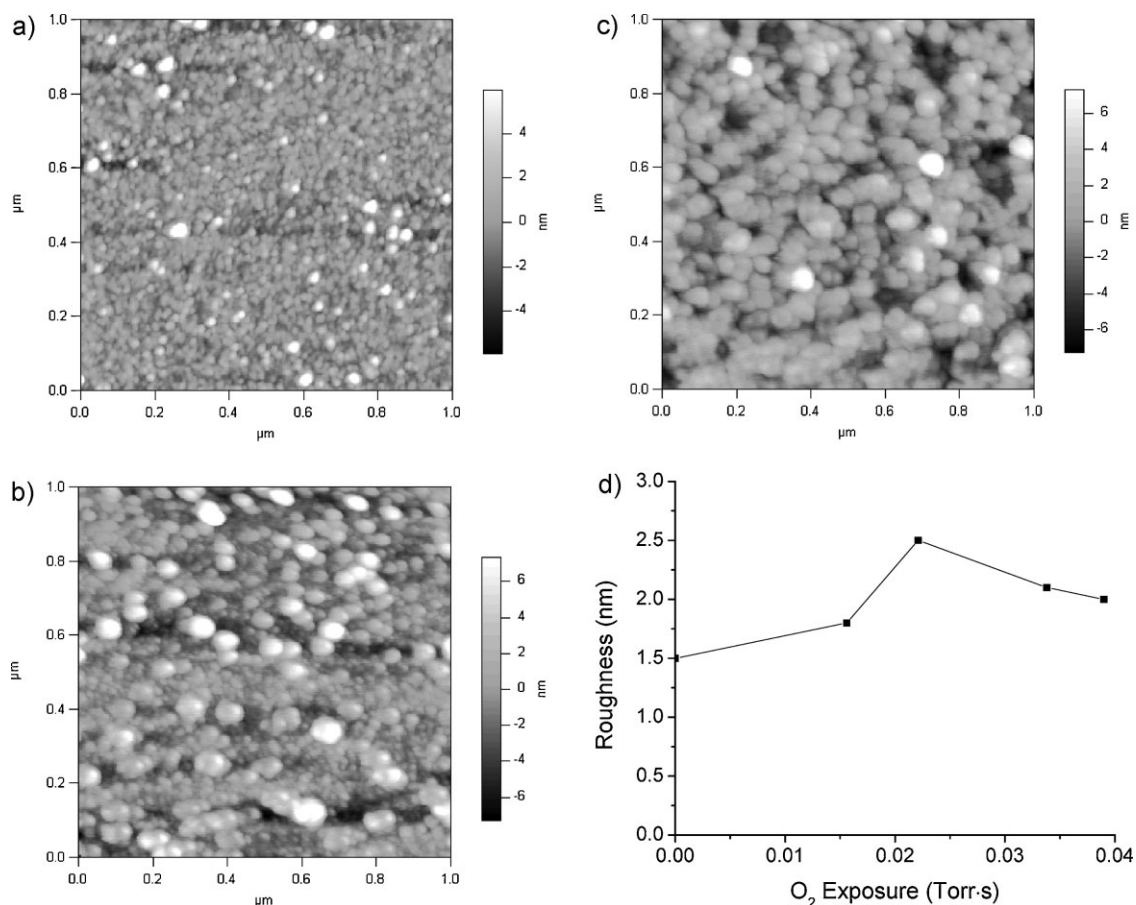


Fig. 9. AFM images of ~ 30 nm Ru thin films deposited at 325°C with various O_2 exposures: a) 0 Torr \cdot s; b) 0.022 Torr \cdot s; and c) 0.034 Torr \cdot s. d) Summary of the rms roughness versus O_2 exposure.

$\lambda = 1.54 \text{ \AA}$ is the wavelength of the Cu $K\alpha$ source, β the width of the peak at half maximum, and θ the peak position. Gaussian fitting of the Ru(002) peak gave $\beta = 0.047^\circ$ and the grain size was calculated to be 25 nm after correcting for the X-ray instrument broadening. These diffraction studies show the film is not strongly oxidized during deposition, which excludes mechanism (3) and suggests that the recombinative desorption of oxygen is the dominant mechanism.

Atomic force microscopy (AFM) images (Figs. 9a–c) of Ru films (~ 30 nm) deposited at 325°C show the grain size increases with O_2 exposure. Without O_2 as the co-reactant, the grains are uniformly small, which produces relatively smooth films with root mean square (rms) roughness ~ 1.5 nm for a ~ 30 nm film. After introducing O_2 , some grains grow bigger and the size distribution becomes non-uniform. When E_{O} is approaching E_{max} , the grain size has a narrower distribution, and the crystallinity is improved. The rms value versus E_{O} is summarized in Figure 9d. The roughness increases from 1.5–1.8 nm to 2.0–2.5 nm due to the improved crystallinity achieved under higher O_2 exposure.

Figure 10a shows that both the resistivity and density of ~ 30 nm Ru films depend on the O_2 exposure. At low exposure (e.g., $E_{\text{O}} < 0.02$ Torr s at 325°C), the film density is

around $7\text{--}8 \text{ g cm}^{-3}$. The density quickly increases with E_{O} and reaches a plateau around the bulk density (12.3 g cm^{-3}) at $E_{\text{O}} \sim 0.33$ Torr s. The film resistivity is more sensitive to O_2 exposure and sharply decreases from $320 \mu\Omega \text{ cm}$ to $14 \mu\Omega \text{ cm}$ with E_{O} from zero to 0.022 Torr \cdot s. Further increasing E_{O} to 0.033 Torr \cdot s decreases the resistivity to $9.4 \mu\Omega \text{ cm}$, which is 32% higher than the bulk resistivity ($7.1 \mu\Omega \text{ cm}$). The thin film resistivity is affected by scattering from GBs, impurities, interfaces, and surfaces.^[19] Because the grain size is approximately equal to the film thickness, the scattering-induced resistivity model can be simplified as Equation 3.^[19]

$$\rho = \rho_0 \left(1 + \frac{t_0}{t} \right), \quad (3)$$

ρ is the thin film resistivity, ρ_0 the bulk resistivity including the effect of impurity scattering, t_0 the characteristic length related to the electron mean free path and scattering effects of GBs, interfaces, and surfaces, and t the film thickness. By linear fitting ρ to $1/t$ (Fig. 10b), we got $\rho_0 = 8.6 \mu\Omega \text{ cm}$ and $t_0 = 6$ nm. Thus the resistivity for thick films is extrapolated to be $8.6 \mu\Omega \text{ cm}$, which is 21% higher than the bulk value. Assuming that both C and O have same scattering effect, the rate of the resistivity increase for these impurities can be

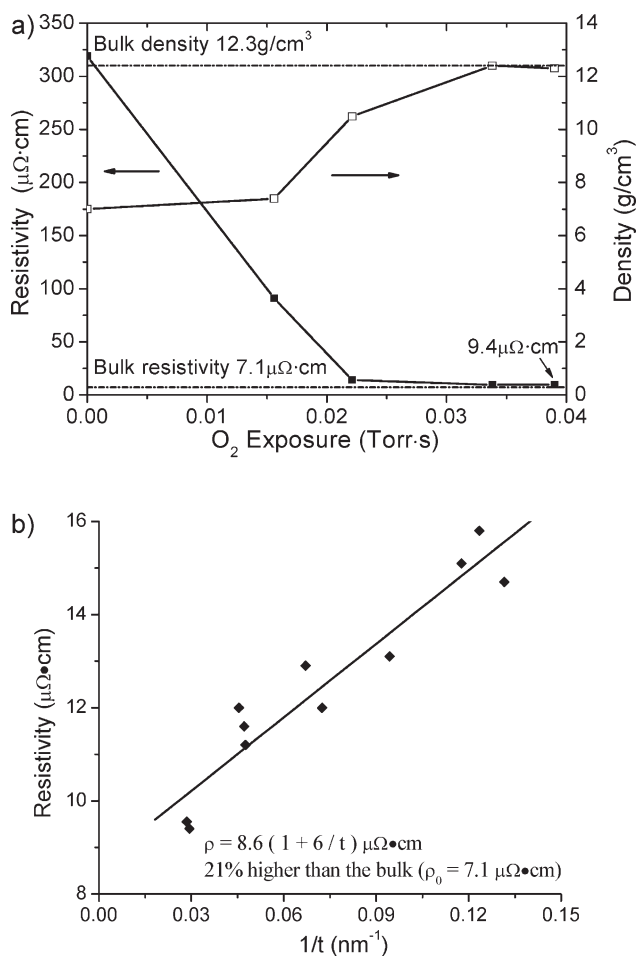


Fig. 10. a) Resistivity and density variation with O₂ exposure for ALD films deposited at 325 °C; b) the thickness dependence of resistivity.

estimated to be $\sim 2 \mu\Omega \text{ cm}$ per at.-%, which is close to the value for bulk Cu ($1 \mu\Omega \text{ cm}$ per at.-%).^[19,20]

The deposition temperature has a less pronounced effect than O₂ exposure. The maximum O₂ exposure for adherent films (E_{max}) increases with the deposition temperature, shown in Figure 11a. The growth rate increases from 0.5 Å per cycle at 300 °C to 1.7 Å per cycle at 400 °C (Fig. 11b). The increase of E_{max} with temperature is clearly related to the high growth rate at high temperature, i.e., more Ru precursor molecules can consume more adsorbed oxygen and lower the oxygen concentration in Ru films. Saturation of the growth rate with increasing temperature was also observed for the Ru(thd)₃ and RuCp₂ systems, which suggests these ALD processes follow a reaction mechanism similar to the one discussed by Aaltonen and co-workers: Ru films are deposited by oxidizing the precursor ligands with dissociatively adsorbed oxygen from the subsurface region.^[4,6] The resistivity is near $10 \mu\Omega \text{ cm}$ for deposition temperatures from 320 °C to 400 °C (Fig. 11b). Figure 12 shows the AFM image of a 35 nm Ru film deposited at 400 °C. Both the roughness (1.9 nm) and crystallinity are similar to the film deposited at 325 °C (Fig. 8c).

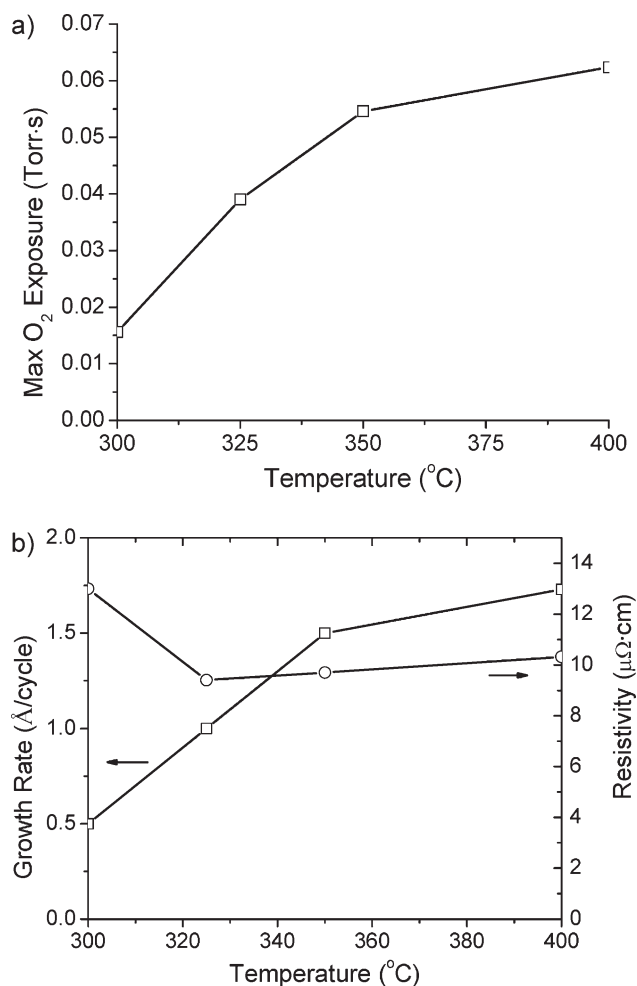


Fig. 11. a) The maximum O₂ exposure at various deposition temperatures; b) the growth rate and resistivity of $\sim 30 \text{ nm}$ Ru films deposited at E_{max} and various deposition temperatures.

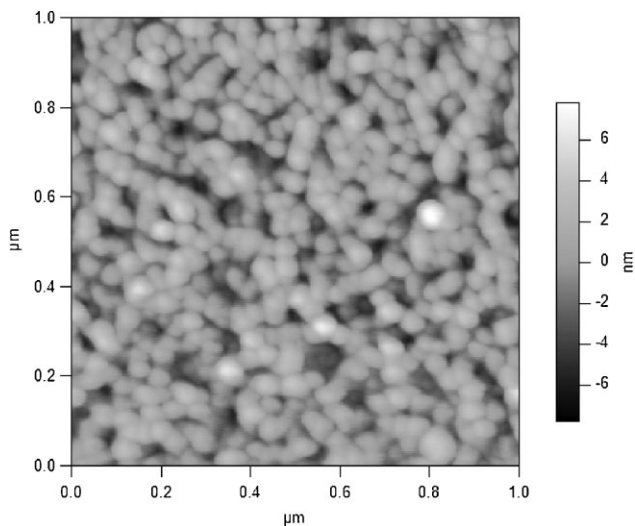


Fig. 12. AFM image of a 35 nm Ru thin film deposited at 400 °C and E_{max} . The rms roughness is 1.9 nm.

3. Conclusions

High quality ruthenium thin films were deposited by ALD with bis(*N,N'*-di-*tert*-butylacetamidinato)ruthenium(II) dicarbonyl and O₂. The film crystallinity, density, and resistivity strongly depend on the O₂ exposure, while the roughness is relatively insensitive to E_O. As E_O ≈ E_{max}, the films have the lowest resistivity, highest density, and best crystallinity (~10 μΩ cm, ~12.3 g cm⁻³ and grain size comparable to film thickness). High deposition temperature leads to higher growth rate, but has less effect on film structures and properties. For deposition temperature in the range 320 °C–400 °C, the resistivity is ~10 μΩ cm and roughness is ~2 nm for 30 nm films. When E_O > E_{max}, films peel off from the substrate due to the recombinative desorption of O₂. The impurities are mainly O (0.27 ± 0.03 at.-%) and C (0.30 ± 0.05 at.-%). The C is mostly segregated along grain boundaries, which are less dense than the grain interiors. The O is more uniformly dissolved in the Ru film. The rate of resistivity increase with impurities is estimated to be ~2 μΩ cm per at.-%, which is comparable to the value of copper (1 μΩ cm per at.-%).

4. Experimental

Ru thin films were deposited in a home-built, flow-type, tube reactor operated at the base pressure of 300 mTorr with bis(*N,N'*-di-*tert*-butylacetamidinato)ruthenium(II) dicarbonyl and O₂. The substrate temperature was measured by a thermocouple inside the sample holder. The Ru precursor was kept in a glass bubbler at 140 °C and delivered to the reactor by N₂ carrier gas added to the head space of the bubbler to a pressure of about 10 Torr. This added N₂ carrier gas, along with the entrained Ru precursor vapor, was released to the reactor in each ALD cycle. High purity O₂ (99.99%) was used as co-reactant and delivered from a 5 mL trap volume with its pressure controlled by an in-line regulator. One ALD cycle consisted of one Ru precursor dose and one O₂ dose with 10 s purging in between. The deposition temperatures varied from 300 °C to 400 °C. All films were deposited on thermal SiO₂ (300 nm)/Si wafers (1 inch by 1.5 inch) with 5 min UV/ozone pre-treatment to remove surface organic contamination.

The film resistivity was calculated from the thickness measured by X-ray reflectivity (XRR) (Scintag XDS2000) multiplying the sheet resistance

measured by a four-point probe. The morphology was studied by SEM (Zeiss FESEM Ultra55) and AFM (Asylum MFP-3D). The crystal structure and phase were determined by XRD (Scintag XDS2000) and electron diffraction (JEOL 2100). The roughness and crystallinity were characterized using AFM and TEM (JEOL 2100). The impurity concentrations and their distribution in the crystallites were measured by APM (LEAP 3000X HR). Impurity analysis was also attempted by XPS (ESCA SSX-100). The ALD Ru film density was obtained from the area density by Rutherford back scattering divided by the film thickness from XRR.

Received: March 5, 2009

Revised: June 01, 2009

- [1] V. Misra, G. Lucovsky, G. Parsons, *MRS Bull.* **2002**, 27, 212.
- [2] O. K. Kwon, J. H. Kim, H. S. Park, S. W. Kang, *J. Electrochem. Soc.* **2004**, 151, G109.
- [3] S. K. Kim, G. J. Choi, S. Y. Lee, M. Seo, S. W. Lee, J. H. Han, H. S. Ahn, S. Han, C. S. Hwang, *Adv. Mater.* **2008**, 20, 1429.
- [4] T. Aaltonen, A. Rahtu, M. Ritala, M. Leskela, *Electrochem. Solid State Lett.* **2003**, 6, C130.
- [5] T. Aaltonen, P. Alen, M. Ritala, M. Leskela, *Chem. Vapor Deposition* **2003**, 9, 45.
- [6] T. Aaltonen, M. Ritala, K. Arstila, J. Keinonen, M. Leskela, *Chem. Vapor Deposition* **2004**, 10, 215.
- [7] H. Z. Li, T. Aaltonen, Z. W. Li, B. S. Lim, R. G. Gordon, *Open Inorg. Chem. J.* **2008**, 2, 11.
- [8] H. Li, D. B. Farmer, R. G. Gordon, Y. Lin, J. Vlassak, *J. Electrochem. Soc.* **2007**, 154, D642.
- [9] S. H. Kwon, O. K. Kwon, J. H. Kim, S. J. Jeong, S. W. Kim, S. W. Kang, *J. Electrochem. Soc.* **2007**, 154, H773.
- [10] H. Over, A. P. Seitsonen, *Science* **2002**, 297, 2003.
- [11] B. Gault, F. de Geuser, L. T. Stephenson, M. P. Moody, B. C. Muddle, S. P. Ringer, *Microsc. Microanal.* **2008**, 14, 296.
- [12] D. N. Seidman, *Ann. Rev. Mater. Res.* **2007**, 37, 127.
- [13] Y. D. Kim, H. Over, G. Krabbes, G. Ertl, *Top. Catal.* **2001**, 14, 95.
- [14] A. Bottcher, H. Niehus, *J. Chem. Phys.* **1999**, 110, 3186.
- [15] R. Blume, H. Niehus, H. Conrad, A. Bottcher, L. Aballe, L. Gregoratti, A. Barinov, M. Kiskinova, *J. Phys. Chem. B* **2005**, 109, 14052.
- [16] A. Bottcher, H. Conrad, H. Niehus, *J. Chem. Phys.* **2000**, 112, 4779.
- [17] S. J. Park, W. H. Kim, W. J. Maeng, Y. S. Yang, C. G. Park, H. Kim, K. N. Lee, S. W. Jung, W. K. Seong, *Thin Solid Films* **2008**, 516, 7345.
- [18] B. E. Warren, *X-Ray Diffraction*, Dover Publications, INC, New York 1990.
- [19] S. M. Rossmagel, T. S. Kuan, *J. Vac. Sci. Technol. B* **2004**, 22, 240.
- [20] J. M. E. Harper, E. G. Colgan, C. K. Hu, J. P. Hummel, L. P. Buchwalter, C. E. Uzoh, *MRS Bull.* **1994**, 19, 23.