

# High Temperature Atomic Layer Deposition of Ruthenium from N,N-Dimethyl-1-ruthenocenylethylamine

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Ruthenium thin films were grown by atomic layer deposition from *N*,*N*-dimethyl-1-ruthenocenylethylamine precursor. The growth was examined in the substrate temperature range of 325–500 °C. The growth rate increased with the substrate temperature but was quite stable between 400 and 450 °C. The films typically consisted of polycrystalline hexagonal ruthenium metal with a resistivity in the range of 10–20  $\mu\Omega$  cm when the film thickness was 10 nm and above. A resistivity of 49  $\mu\Omega$  cm could be achieved in the film as thin as 4 nm. Measurements on Al/Al<sub>2</sub>O<sub>3</sub>/Ru metal-insulator-metal (MIM) capacitors with Ru films as metal electrodes revealed a capacitive voltage behavior typical of MIM structures and appreciably high breakdown voltages. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3251285] All rights reserved.

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The development of micro- and nanoelectronic device generations has driven the search for advanced deposition processes, enabling the growth of thin metal layers<sup>1-3</sup> applicable as electrodes in memory capacitors and field-effect transistors. Efforts have been made to integrate high work-function metals, in particular ruthenium,<sup>3-9</sup> with the gate and memory capacitor technologies. Ruthenium thin films for microelectronics, apart from a few physicalvapor-deposited exceptions,<sup>8,9</sup> have mainly been grown by chemical vapor deposition (CVD).<sup>3,4,10-15</sup> Besides CVD, atomic layer deposition (ALD)<sup>1</sup> has been investigated to find the most feasible way to grow uniform, dense, and conductive Ru films to thicknesses of just a few nanometers over substrates of arbitrary configuration.

Ru films have been grown by ALD and related techniques from a variety of precursors, such as  $Ru(acac)_3$  and  $Ru(thd)_3$ ;<sup>2,1</sup> bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)Ru, i.e.,  $Ru(thd)_2COD;^5$  bis(N,N'-di-tert-butylacetamidinato)ruthe-nium(II)dicarbonyl, i.e.,  $Ru('Bu-Me-amd)_2(CO)_2;^{18}$  ruthenocenes: dicyclopentadienylruthenium,  $\operatorname{RuCp}_{2}^{19-21}$  bis(ethylcyclopentadienylruthenium,  $\operatorname{RuCp}_{2}^{21,22}$  and (cyclopentadienyl)(isopropylcyclopentadienyl)ruthenium, CpRu(i-PrCp).<sup>7</sup> In most cases, processes at rather low deposition temperatures, not exceeding 300–350°C,<sup>5,16,18,19,21</sup> have been realized and reported. The roughness of ruthenium films increases with the thickness and growth rate accompanied by higher growth temperatures.<sup>16</sup> The highest ALD temperatures examined have typically been 350-400°C, whereas at higher temperatures, e.g., 450°C, the growth becomes enhanced and probably less controlled due to the thermal decomposition of the precursor.<sup>16</sup> However, some CVD studies have been targeted at higher temperatures, e.g., 450–480°C.<sup>12,14</sup> Ruthenocenes were examined in the CVD of Ru at least a couple of decades ago,<sup>2</sup> with the best film properties achieved at 575°C in O<sub>2</sub>, although they remain inferior to those achieved when using pyrolysis of carbonylbased precursors at 300°C. In regard to the choice of deposition temperature, low temperatures may be recommended due to the lowered thermal budget and the lowered tendency to react with the substrate. Thermally, more stable metal precursors may allow the growth of films with chemically and structurally higher purity. In ruthenium, the nucleation and adhesion properties may also occur rather strongly dependent on the deposition temperature and actually improve with the increase in substrate temperature. Also, the growth rate generally increases with the temperature.<sup>2,11,16,19</sup> In ALD with metallorganic precursors, the upper limit for the deposition temperature is set by self-decomposition of the precursors.

In this study, ALD of Ru was realized between 325 and 500°C using *N*,*N*-dimethyl-1-ruthenocenylethylamine  $C_5H_5$ -Ru- $C_5H_4$ -CH(CH<sub>3</sub>)N(CH<sub>3</sub>)<sub>2</sub>, also known as [1-(dimethylamino)ethyl]ruthenocene, as a ruthenium precursor (Fig. 1). The precursor may

further be denoted as N,N-RuCp. Ru was formed via oxidative decomposition<sup>9,20</sup> of the metal precursor by air pulses. Primary ALD behavior, including growth rate as a function of the substrate temperature, growth rate against Ru precursor pulse length, and film thickness vs amount of growth cycles, was studied. In addition, the conductivity and structure of Ru films were evaluated as well as their possible dependence on the film morphology and thickness. The study has thus been devoted to the clarification of the feasibility of ALD with the precursor selected.

#### Experimental

*N*,*N*-RuCp (Fig. 1), obtained from Honeywell International, Inc.,<sup>24</sup> was evaporated from an open boat inside a commercial hotwall flow-type ALD reactor F120 (ASM Microchemistry).<sup>25</sup> The other reactant was air with a flow rate of 25 sccm. N<sub>2</sub> (99.999%) was used as the carrier gas. The *N*,*N*-RuCp evaporation temperature was 75–80°C. The precursor was initially a gray solid but melted upon heating inside the boat. The growth of Ru was examined in the substrate temperature range of 325–500°C. The *N*,*N*-RuCp and air pulse lengths were varied between 1 and 10 s, while the purging times were kept constant at 1 s. The sequence consisting of the *N*,*N*-RuCp-pulse–purge–air-pulse–purge were denoted as cycle time sequence 1-1-1-1 s, for instance.

Ru films were deposited on an  $Al_2O_3$  nucleation layer grown at the same temperature from  $Al(CH_3)_3$  and  $H_2O$  on  $SiO_2/Si$  and soda lime glass substrates with 200 cycles and cycle times of 0.2-0.5-0.5-0.5 s for the sequence  $Al(CH_3)_3$ -pulse–purge- $H_2O$ –purge.  $Al_2O_3$ served as a suitable starting surface enhancing the nucleation density and growth rate of Ru.<sup>16,26</sup>

The film structure was determined by a Bruker D8 Advance X-ray diffractometer either in grazing incidence X-ray diffraction (GIXRD, incidence angle was 1°) mode or  $\Theta$ -2 $\Theta$  mode. The film thicknesses were measured either by X-ray reflectance (XRR) or by an energy-dispersive X-ray (EDX) spectrometer connected to a scanning electron microscope (SEM) apparatus, Hitachi S-4800. SEM was also exploited for visualization of the Ru surface morphology.

The resistivity of Ru films was evaluated by a four-point probe Cascade Microtech C4S-44. Electrical measurements were also carried out on Al/Al<sub>2</sub>O<sub>3</sub>/Ru capacitor structures at room temperature after the E-beam evaporation of a shadow-masked array of aluminum top electrodes with an area of 0.204 mm<sup>2</sup>. The capacitance–voltage (*C-V*) curves were recorded using an HP4284A precision LCR meter in a two-element series circuit mode with a trigger delay time of 0.5 s. The ac voltage applied to the capacitor was 0.05 V, while the frequency of the ac signal was held at 1 MHz. The current–voltage curves were measured with a Keithley 2400 source meter in the stair sweep voltage mode with a voltage step of 0.05 V.

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Figure 1. Schematic representation of C<sub>5</sub>H<sub>5</sub>-Ru-C<sub>5</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)N(CH<sub>3</sub>)<sub>2</sub>.

#### **Results and Discussion**

*Film growth.*— Figure 2 depicts the behavior of film growth rate against substrate temperature. At relatively low temperatures below  $350^{\circ}$ C, the *N*,*N*-RuCp precursor did not provide efficient growth. Uniform films were obtained only at  $375^{\circ}$ C and above. For comparison, in the same reactor, the onset temperature of Ru ALD on Al<sub>2</sub>O<sub>3</sub> has been  $325^{\circ}$ C for Ru(thd)<sub>3</sub><sup>16</sup> and as low as  $275^{\circ}$ C for RuCp<sub>2</sub>.<sup>19</sup> Thus, the *N*,*N*-RuCp precursor appears to be a "high temperature" ALD precursor. Between 400 and 450°C, the growth rate occurred appreciably stable against the temperature, and a relatively fast growth of uniform films was provided.

At 400°C, the film growth rate was independent of the N,N-RuCp pulse length varied in the range of 1–5 s (Fig. 3), indicative of the self-limiting growth characteristic of ALD. Remarkably, the growth rate did not also increase with the N,N-RuCp pulse length at 450 and even at 500°C, referring to the appreciably high thermal stability of the Ru precursor. At 500°C, the sudden increase in the growth rate (Fig. 2) might thus be due to the more effective mechanism of oxidative decomposition of N,N-RuCp. Thus, the growth rate behavior resembles that of a typical ALD model with an initial increment in the growth rate upward from the reaction threshold temperature, then reaching a "plateau" of width characteristic of a particular ALD process with nearly temperature-independent adsorption and surface reaction rates (400–450°) and with some thermal decomposition above that.

Retardation of the nucleation during the first growth cycles is a rather common feature in ALD of noble metals, also observed in studies on ALD of Ru,<sup>16,21</sup> even in the plasma-assisted process.<sup>22</sup> The nucleation delay is dependent on growth temperature and process parameters, also quite likely on the precursors used. The growth process described in the present study seemed to have quite a short nucleation delay of about 100 cycles (Fig. 4). The nucleation time may be shortened in terms of the amount of cycles by increasing the



Figure 3. Ru film growth rate as a function of the Ru precursor pulse length at different temperatures.

length of air pulse, but this is achieved with the expense of the deposition time, i.e., it causes the prolongation of the cycle. However, the growth during 1 cycle is certainly enhanced by a longer air pulse.

*Film structure.*— The GIXRD measurements showed that the films consisted of metallic Ru showing two major 002 and 101 and the weaker 100 reflection (Fig. 5). The X-ray diffraction (XRD) patterns of Ru grown from *N*,*N*-CpRu can be regarded as rather typical of Ru films and quite similar to those grown by CVD  $^{4,11}$  or ALD.<sup>16,21</sup> A simultaneous appearance of weaker 100 and stronger 002 and 101 reflections is indicative of the formation of polycrystalline hexagonal ruthenium according to the powder diffraction file 06-0663.

The thinnest films (4 nm) grown in the present study were apparently amorphous or at least amorphous to GIXRD. The crystal growth was enhanced by the increasing deposition temperature as well as film thickness. Also, the intensity ratio of the 002 and 101 reflections increased from 0.47 to 1.14, with the growth temperature ranging from 350 to 400°C, which is indicative of some changes in preferential orientation.

The orientation of Ru thin films was further studied by XRD patterns recorded using the  $\Theta$ -2 $\Theta$  geometry that detects only those lattice planes that are parallel to the film surface (Fig. 5). Texturing is evident, as the 002 reflection is clearly the dominant one in the patterns. The 002/101 intensity ratio probably depends mainly on the deposition temperature and somewhat also on the film thickness. In the thin films (ca. 10 nm) grown at 450°C (Fig. 5), the 101 reflection was hardly detected. One can see that the (001) orientation



Figure 2. Ru film growth rate against growth temperature.



**Figure 4.** Ru film thickness as a function of the growth cycles with different air pulse lengths at 400°C. The film thickness was measured by EDX in the middle of the substrate (at ca. 2.5 cm distance from the leading edge).



2⊖, degree

**Figure 5.** Representative X-ray diffractograms of Ru films grown at different substrate temperatures, measured in GIXRD mode (uppermost panel); Ru films grown to variable thickness or with different Ru precursor pulse length, measured in GIXRD mode (the second panel); Ru films grown at different substrate temperatures to different thicknesses, measured in  $\Theta$ -2 $\Theta$  mode (the third panel); and thin Ru films grown at 450°C, measured in  $\Theta$ -2 $\Theta$  mode (bottom panel). Inset depicts an XRD pattern from a film grown at 500°C. Ru peaks are denoted with corresponding Miller indexes. Labels denote the amounts of ALD cycles used, cycle times, growth temperatures, diffraction peak intensity ratios, and film thicknesses, *d*.

truly becomes preferred in ruthenium films, whereas the 101 reflection is the most intense one, according to the powder diffraction files.

The crystallographic orientation in Ru films may depend on the choice of precursor. For instance, Kawano et al.<sup>27</sup> studied metallorganic chemical vapor deposition (MOCVD) of ruthenium at rather high temperatures, up to 400°C, from three precursors: bis(2,4-dimethylpentadienyl)ruthenium, i.e., Ru(DMPD)<sub>2</sub>; (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)ruthenium, i.e., Ru(DMPD)(EtCp); and bis(ethylcyclopentadienyl)ruthenium, i.e., Ru(EtCp)<sub>2</sub>. XRD demonstrated a strong, dominant 002 reflection in the films grown from Ru(DMPD)<sub>2</sub>, analogous to the results of the present study, whereas in the case of other two precursors, the 101 reflection also remained of high significance. The (001)-oriented films grown from Ru(DMPD)<sub>2</sub> possessed a lower resistivity at all deposition temperatures compared to the films grown from Ru(D-MPD)(EtCp) and Ru(EtCp)<sub>2</sub>.

The formation of ruthenium oxide was not recognized in the present study. For comparison, Papadatos et al.<sup>12</sup> investigated the MOCVD of ruthenium from Ru(EtCp)<sub>2</sub> at temperatures ranging from 320 to 480°C. According to their results, the formation of RuO<sub>2</sub> was dependent on the oxygen flow rate. At 50 sccm, the film resistivity remained at the level characteristic of metallic Ru, whereas at 300 sccm, the resistivity started to increase at deposition temperatures of 380-400°C and higher. Futhermore, XRD distinctively revealed the formation of pure RuO<sub>2</sub> phase at 480°C, whereas at 400°C, the film consisted of Ru metal with competing 100 and 101 peaks.<sup>12</sup> Even in the ALD processes conducted at markedly lower temperatures, the formation of RuO<sub>2</sub> can become favored under appropriately modified conditions. For instance, Kim et al.<sup>4</sup> achieved RuO<sub>2</sub> films while exposing the substrate continuously to oxygen as a constituent of the carrier gas, i.e., also simultaneously with Ru(EtCp)<sub>2</sub> pulses at 265°C. In addition, Kwon et al.<sup>29</sup> studied the stacking of RuO<sub>2</sub> films on Ru at 270°C from Ru(EtCp)<sub>2</sub> and found that the formation of RuO<sub>2</sub> is dependent on the reactor pressure.  $RuO_2$  was grown when the total process pressure exceeded 2 Torr with 55% of  $O_2$  in the carrier gas, flowing with a rate of 100 sccm. In the present study, the air injection flow rate was 25 sccm (N<sub>2</sub> carrier gas flow rate was 400 sccm), and it was not constant but pulsed as characteristic to ALD. RuO2 was not detected even in the films grown at 500°C. At 500°C, the (001) orientation remained dominant, although with a complementary reappearance of weaker 101 peaks (Fig. 5). It seems that the application of a pulsed and moderate air/oxygen flow in the ALD process and a precursor chemistry favoring textured and (001)-oriented Ru growth appears to be advantageous in terms of the structural stability at higher temperatures as well as appreciably low resistivity.

*Film morphology.*— SEM images of selected Ru films are shown in Fig. 6. The images reveal a clear development of the nucleation density and morphology upon changes in substrate temperature and film thickness. By comparing the films grown using only 100 cycles at 400, 450, and 500°C (left column in Fig. 6), one notices that the nucleation density decreases with an increase in the growth temperature. At 500°C, the films appeared to be discontinuous, consisting of separated islands, and thus did not conduct under the four-point probe. At 450°C, the films were somewhat electrically conducting, i.e., the islands were partially coalesced after 100 cycles. At 400°C, 100 cycles were evidently sufficient to deposit moderately conducting films, although a somewhat increased air pulse length was needed to increase the nucleation density. Even at 400°C, voids were observed between the continuous regions of the film.

At 400°C, an increase in the amount of ALD cycles to 200 provided continuous, although pinhole-rich, 7 nm thick films with a resistivity of around 20  $\mu\Omega$  cm (middle panel in the upper row in Fig. 6). Further increment in the amount of cycles, however, often resulted in a strong increase in the roughness, mainly caused by the



Figure 6. Selected representative SEM images of Ru films grown at 400°C (upper row), 450°C (middle row), and 500°C (bottom row). Labels indicate the deposition temperature, amounts of growth cycles, cycle times, Ru thicknesses, and resistivities.

partial detachment of the film from the substrate surface, i.e., partial delamination. The large features observable on the surface of the film grown at 400°C with 500 cycles are delaminated areas in a bird's-eye view. Delamination and roughness may be regarded as issues in the Ru growth process, and the thickness of Ru films should thus be optimized at any temperature chosen to find a trade-off between discontinuity and adhesion problems.

At 450°C, continuous and conductive layers were formed after 200 growth cycles (the middle row in Fig. 6). The amount of voids detected was negligible. At 500°C, 200 growth cycles did not suffice for the formation of continuous layers, although the islands became partially coalesced (the bottom row in Fig. 6), similar to what was observed at 450°C after 100 cycles. Thus, the films became conductive. At 500°C, the effect of the N,N-RuCp pulse length to the nucleation density of Ru occurred quite strongly. The prolongation of the Ru precursor pulse from 2 to 6 s dramatically improved the film's continuity and conductivity, despite some pinholes still visible. Longer precursor pulses may assist well in achieving better coverage of the substrate surface with precursor molecules, which may then become an essential factor at the earliest growth stages, i.e., during the growth of the nanometers. The denser the initial molecular layer, the higher the probability of the formation of the continuous film.

The XRR measurements revealed that, at  $450^{\circ}$ C, the roughness decreased slightly from 1.0 to 0.8 nm with the pulse time increasing from 2 to 6 s, supporting the results of the SEM inspection (middle row in Fig. 6) of the same samples. At  $500^{\circ}$ C, the roughness decreased from 2.5 to 1.6 nm, with the pulse time increasing from 2 to 6 s. Thinner films (5–6 nm) demonstrated considerable roughness, ca. 1.6–1.7 nm, at both temperatures due to the formation of islands. Analogous trends applied for density, also measured by XRR, which increased from 3–7 to 9–11 g/cm<sup>3</sup> with thickness. Thus, in the thicker films, the density approached that of the bulk (12 g/cm<sup>3</sup>). The film density tended to be slightly higher in films grown with 6 s pulse length compared to those grown with shorter pulses. For comparison, roughness and density values obtained in this study are quite similar to those of Ru films grown from beta-diketonate precursor by atomic vapor deposition.<sup>2</sup>

At elevated substrate temperatures (450–500 °C), delamination is not to be considered as the major morphological problem. The time required for the coalescence of islands has clearly been increased at such high temperatures. The controlled formation of separated islands may not necessarily be a drawback but may serve as a basis for the deposition of nanodot-based flash memory structures.<sup>18</sup>



Figure 7. Dependence of Ru film thickness and resistivity on the amount of ALD cycles. Lines are guides for the eyes.

However, because the roughness increased with temperature as well as with thickness, the deposition of Ru at the highest temperature  $(500^{\circ}C)$  should be treated as the most sensitive to the variations in the amount of cycles and cycle parameters. Such dependences of roughness and growth rate on temperature are not unique; the analogies have been met in the Cp-based CVD<sup>11</sup> and ALD Ru processes.<sup>19,22</sup> The thickest films (ca. 60 nm) grown in the present study at both 450 and 500°C demonstrated dramatically roughened surfaces (not shown) compared to thinner films. However, the delamination was not recognized at 450 and 500°C as clearly as at 400°C, which may also be due to the different thicknesses.

Ruthenium films may delaminate due to the differences in thermal expansion coefficients between the metal and oxide nucleation layer or silicon substrate. It was noted earlier that ruthenium electrode films, deposited in a relatively fast sputtering process, can be easily delaminated after a long-term annealing in a nonoxidizing inert atmosphere, whereas the annealing in oxygen and at least partial formation of  $RuO_2$  retained the adhesion.<sup>9</sup> In the present study, no crystallographic traces of  $RuO_2$  were noticed even in the films grown at elevated temperatures in the relatively slow ALD process mainly proceeding under nitrogen flow.

The nucleation behavior of Ru films observed in this study can be regarded as quite common for ALD of noble metals, although affected by the substrate as well as growth parameters. For instance, nucleation rate and density can be enhanced by using plasmaassisted ALD process<sup>22</sup> or the thermal growth realized on more ionic oxide surfaces,<sup>4</sup> which also were more crystalline compared to Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Nevertheless, the growth of Ru films most commonly starts with the formation of nanodots or islands of variable density, and the formation of continuous metal layers proceeds via clearly detectable, somewhat time-consuming, coalescence of islands.

Film resistivity.— The resistivity of Ru films thicker than about 10 nm, i.e., those grown by using at least 200 ALD cycles, quite reproducibly approached 20  $\mu\Omega$  cm and values below that. The resistivity, although correlated with the film thickness (Fig. 7), always remained 2–3 times larger than the bulk resistivity. The fact that the conductivity of the 7–23 nm thick Ru films remains lower than that of the bulk ruthenium is not surprising. Thin films consist of fine grains, actually nanocrystallites. These crystallites have grain boundaries and voids between them, and their size may well be decreased below the limit of the free transport path of the electrons, scattering at interfaces and surfaces, also at possible impurities. Therefore, the resistivity is expected to increase with the decreasing film thickness and, in such thin films, bulk resistivities cannot be reached. Also in thicker films (30–50 nm) grown in the present study, the resistivity never dropped below 12–15  $\mu\Omega$  cm, probably



**Figure 8.** Dependence of film thickness and resistivity on the pulse length at  $400^{\circ}$ C. The amount of pulses was 200. The *N*,*N*-RuCp pulse length was 2 s and the purge time was 1 s. Lines are guides for the eyes.

due to the increased surface roughness. For comparison, 22–36 nm thick Ru films grown from beta-diketonates have possessed resistivities of 11.5–15.1  $\mu\Omega$  cm, not directly correlated with the film thickness but rather to the process.<sup>2</sup> Even somewhat higher resistivities exceeding 20  $\mu\Omega$  cm were obtained in a plasma-enhanced process using RuCp<sub>2</sub> and Ru(EtCp)<sub>2</sub> precursors.<sup>21</sup> Resistivities close to the bulk value have seldom been measured in Ru films. For instance, resistivities as low as 10  $\mu\Omega$  cm have been reported for the films grown from Ru(DMPD)<sub>2</sub><sup>11</sup> at 400°C. Unfortunately, no information about the film thickness as well as roughness effects was revealed in the latter case.

The resistivity of Ru films deposited using N,N-RuCp precursor depended on the air pulse length. At 400°C, the resistivity of the films grown using 200 cycles quite clearly decreased from 21 to 11  $\mu\Omega$  cm with the increase in the air pulse length from 1 to 5 s (Fig. 8). This is due to the increase in the nucleation density and Ru growth rate with the pulse length. At the early stages of the formation of metallic films, the nucleation density becomes most critical: The higher the nucleation density, the faster the formation of continuous metal layers, and the layer would electrically conduct and lower thicknesses. Air pulse lengths higher than 5 s did not bring any further advantage either in terms of growth rate or conductivity (Fig. 8). Regarding the growth rate, this is a sign from the selflimitation of the oxidative decomposition reaction. The resistivity was just slightly increased in the films grown using air pulse lengths exceeding 5 s. Thus, too long air pulses might possibly result in partial oxidation of Ru, although the oxide was not recognized by XRD.

Rather low resistivities can be achieved at quite early stages of Ru growth. For instance, the 4 nm thick Ru film with a resistivity of 49  $\mu\Omega$  cm was grown at 400°C using only 150 cycles with times of 2-1-1-1 s. With 100 cycles and air pulse length increased to 2 s, the resistivity of the resulting film of approximately the same thickness was 67  $\mu\Omega$  cm. Also considering the resistivities in the range of 10–20  $\mu\Omega$  cm, described above for the films grown using 200 ALD cycles, one can conclude that the conductivity of Ru films grown from *N*,*N*-RuCp would be sufficient for their application in metal-insulator-metal (MIM) capacitor structures.

Behavior of Ru as bottom electrode for dielectric oxide.— Special growth experiments were arranged to fabricate MIM capacitors to examine the applicability of 10–15 nm thick Ru films as bottom electrodes. Soda lime glass covered with an Al<sub>2</sub>O<sub>3</sub> (200  $\times$  0.2-0.5-0.5 s cycles) buffer layer served as a substrate. Ru was deposited at 400°C using 150  $\times$  2-1-5-1 s growth cycles. Al<sub>2</sub>O<sub>3</sub> was then grown at the same temperature as the MIM dielectric using 500  $\times$  0.2-0.5-0.5-0.5 s growth cycles. XRR measurements revealed the Ru and Al<sub>2</sub>O<sub>3</sub> layer thicknesses of 10.2 and 34.2 nm, respectively.



**Figure 9.** *C-V* and dissipation–voltage (upper panel) and leakage currentdensity–voltage curves (lower panel) of Al/Al<sub>2</sub>O<sub>3</sub>/Ru MIM capacitors.

Electrical measurements indicated characteristic MIM performance (Fig. 9). One could see that the capacitors were wellinsulating and measurable, showing parameters typical of  $Al_2O_3$  dielectrics. The effective permittivity of the  $Al_2O_3$  film was 7.8. The breakdown field ranged between 3.5 and 4.4 MV/cm. The performance of capacitors is analogous to that observed earlier with 60–80 nm thick Ru films grown from RuCp<sub>2</sub>.<sup>30</sup> Therefore, continuous, appreciably smooth, and thin (10 nm) Ru films grown by ALD from *N*,*N*-RuCp perform well as MIM electrodes.

#### Conclusion

Ruthenium precursor N',N-dimethyl-1-ruthenocenylethylamine C<sub>5</sub>H<sub>5</sub>-Ru-C<sub>5</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)N(CH<sub>3</sub>)<sub>2</sub> was examined in the ALD process in the substrate temperature range of 325–500°C with an acceptable rate between 350 and 500°C. Ruthenium grew as a nonoriented hexagonal phase on Al<sub>2</sub>O<sub>3</sub>/Si substrates. The crystal growth was, quite expectedly, enhanced at high substrate temperatures and with increasing film thickness. The surface roughness also increased with both substrate temperature and film thickness.

The most suitable growth temperatures were 400 and 450°C, noticeably higher compared to most of the previously examined Ru precursors. The growth rate per cycle did not increase with pulse length at 400 and 450°C, referring to the stability of the precursor. High deposition temperatures may partially assist in the suppression of the blistering or the delamination of metal layers from the seed oxide layer. High deposition temperatures enabled the reduction in the length of nucleation time down to 150 ALD cycles, enabling the growth of 3-6 nm thick films with a measurable resistivity of 50–200  $\mu\Omega$  cm even with relatively short pulses (2 s). Longer pulse times (2-6 s) applied during 100-125 ALD cycles deposited 10 nm thick Ru films with resistivities between 10 and 20  $\,\mu\Omega\,$  cm. The resistivities of 10-23 nm thick Ru films grown at 400-500°C were typically 13–14  $\mu\Omega$  cm. Capacitors created from Al/Al<sub>2</sub>O<sub>3</sub>/Ru stacks reliably demonstrated the measurable electrical properties characteristic of MIM structures.

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