Grain Structure – Resistivity Relationship of Ru ALD Precursors

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Introduction

The atomic layer deposition of ruthenium has been previously reported with a wide variety of precursors. However, the search for a Ru ALD process that can deposit a film with a resistivity close to that of bulk Ru (~7 μΩ·cm) is ongoing, with an emerging interest in processes that can selectively deposit low-resistance Ru films. In this work, the grain structure and resistivity relationship for Ru ALD precursors $Ru(IHD)_2(CO)_2$ and $Ru(CpEt)_2$ using O_2 as a co-reactant is investigated using electrical measurements by four-point-probe, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction/reflectometry (XRD/XRR).

Background & Experiment

Ru is viewed as an alternative to Cu and Co interconnect layers at M0/M1 due to its lower effective resistivity in highly-confined vias; additionally, Ru's low diffusion into even porous low-K dielectrics removes the need for a barrier layer, further decreasing effective resistivity[1,2]. A wide variety of atomic layer deposition (ALD) precursors are available, but a highly-selective process for nucleation only on metal surfaces is desired both to eliminate patterning and to allow for the bottom-up fill forming vertically-oriented grains, further improving via conductivity by reducing the presence of grain boundaries[3].

In this report, Ru ALD was performed using two different precursors, $Ru(IHD)_2(CO)_2$ ("Ru-Carish", Tanaka Kikinzoku Int'l.) and $Ru(CpEt)_2$ (Strem Chemicals), with O_2 as a co-reactant at 300 °C deposition temperature at a pressure of ~1 Torr on both SiO_2 and HF-cleaned Si substrates. Prior to deposition, samples were degreased and dipped in 0.5% HF solution for 30 seconds, followed by a 30 minute ultra-high vacuum anneal at 350 °C to remove atmospheric contaminants. After deposition, samples are transferred without breaking vacuum to a UHV chamber for X-ray photoelectron spectroscopy (XPS, Scienta Omicron). 4-point-probe (Ossila Four-Point Probe System, Ossila, Ltd.) measurements were performed after deposition was completed. The film dimensions were 6 mm x 2 mm with a probe spacing of 1.27 mm, which required in a geometric factor of 0.3443 being applied to the sheet resistance to correct for the proper sheet resistance due to the semi-infinite approximation being invalid. Finally, X-ray diffraction/reflectometry (XRD/XRR) were performed on the films to determine film thickness and grain structures.

Ru-Carish Conductivity & Grain Structure

A study was performed to determine the effect of oxygen and grain size on Ru film resistivity. Fig. 1 illustrates the effect of Ru-Carish dose amount on the film resistivity and oxygen level. After 150 cycles, the film is fully buried with both 2 and 4 Ru-Carish pulses per cycle on both Si and SiO_2, but the resistivity on the film with 2 pulses/cycle was roughly 80% higher than with twice the Ru-Carish dose. Previous studies of Ru ALD using oxygen as co-reactants have observed that the mechanism of deposition with oxygen involves the presence of adsorbed oxygen, which when combined with additional Ru precursor can encourage more complete nucleation per cycle and lower oxygen content, decreasing film resistivity[4].

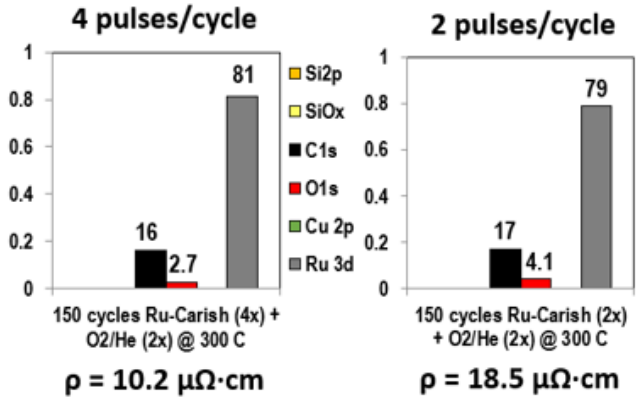

Fig. 1. Effect of Ru-Carish pulses on Ru resistivity. At 300 °C, after 150 cycles at 2 pulses per cycle of Ru-Carish, the film contains roughly 4.1% O, with a resistivity of 18.5 μΩ·cm. Doubling the number of pulses reduces the percentage to 2.7%, with a decrease in resistivity to 10.2 μΩ·cm.

Fig. 2 illustrates the relationship between film thickness and resistivity with 4 pulses per cycle. X-ray reflectometry (XRR) was used to determine film thicknesses for the thinner films (50 cycles and 150 cycles), while cross-sectional SEM was used to determine the 500 cycle film thickness. At 300 °C and 4 Ru-Carish pulses per cycle, the growth rate was determined to be roughly 0.25 nm/cycle, with low oxygen persisting down to a films thickness of 15.7 nm. Four-point-probe sheet resistance measurements showed resistivities of 10.9, 10.8, and 10.7 μΩ·cm for 130 nm, 44 nm, and 16 nm films, respectively. X-ray diffraction measurements show grain sizes for the Ru(101) crystal facets of 24.0, 20.8, and 28.9 nm for each film, respectively, using the Scherrer equation assumption of peak broadening.

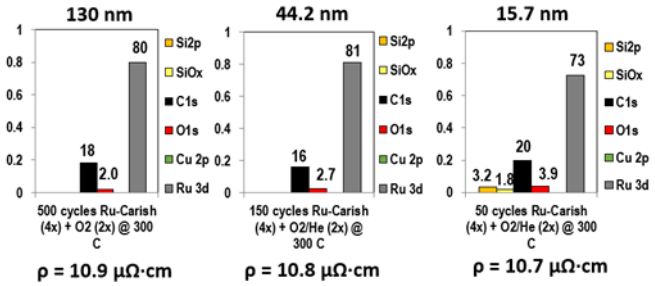

Fig. 2. Resistivity-thickness relationship for Ru ALD. At 300 °C and 4 pulses/cycle, the growth rate was determined to be 0.25 nm/cycle, with low oxygen persisting to 15.7 nm film thickness. Thickness measurement for the 130 nm film was performed via cross-sectional SEM, while thicknesses for the 44.2 and 15.7nm films were determined via XRR. Four-point-probe resistance measurements showed resistivities of 10.9, 10.8, and 10.7 μΩ·cm, respectively.

Ru(EtCp)$_2$ Conductivity & Grain Structure

Next, a cyclopentadienyl-based precursor, Ru(EtCp)$_2$, was used with O_2 as a co-reactant. As opposed to the Ru-Carish precursor, the lack of carbonyl groups that can desorb readily gives finer control over the growth of the film at the cost of requiring finer control over oxygen dosing to ensure all cyclopentadienyl ligands are reacted away without further oxidizing and etching back the Ru film. Fig. 3 illustrates the effect of increased oxygen dosing on resistivity and grain structure. After 350 cycles, the film is fully buried with both 2 and 4 pulses per cycle of O_2 on SiO_2. However, while growth of the film on SiO_2 was continuous and low-resistivity, the film on HF-cleaned Si was high-resistivity and XPS studies of the growth show a significantly-slower growth rate on Si, suggesting a highly-selective Ru metal process with preference to SiO_2 over Si.

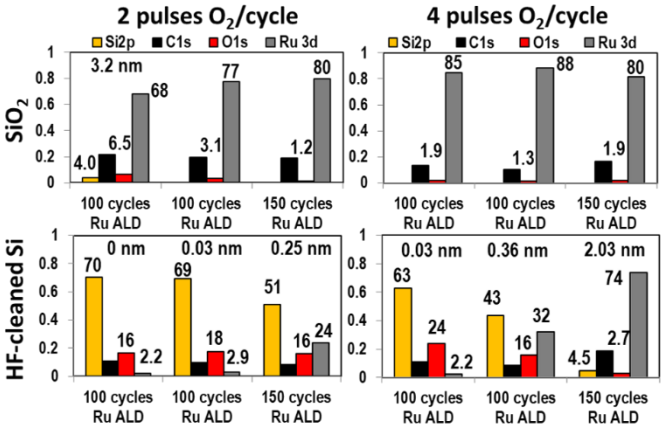

Fig. 3. Substrate selectivity during Ru ALD on SiO_2 and Si. At 300 °C and 2 pulses of O_2, the first 100 cycles deposited results in a 3.2 nm Ru film on SiO_2, with a near-zero thickness on HF-cleaned Si. At the target of 350 cycles, only 0.25 nm was deposited on HF-cleaned Si despite XRR showing a 30 nm Ru film on SiO_2. Doubling the number of O_2 pulses increased the growth rate on HF-cleaned Si, but the growth rate remained significantly lower, with only 2 nm on Si after 350 cycles.

In Fig. 3, attenuation of the substrate during XPS was used to estimate Ru thickness during the first 100 cycles, the next 100 cycles, and the final 150 cycles. With 2 pulses of O_2/cycle, only 0.25 nm was deposited on Si after 350 cycles. Doubling the O_2 dose to 4 pulses increased the growth rate on Si, yet selectivity remained high compared to SiO_2. Unlike all other reports of Ru selective ALD, no passivant was employed.

Fig. 4 illustrates the effect of increased oxygen dosing on resistivity and grain structure. The grain size relationship for the Ru(EtCp)$_2$-deposited Ru films shows an Ru(002) dominant grain structure. While the Ru(002) grain size is roughly constant for the two oxygen dose conditions at 25 nm, the Ru(101) grain size average increases from 18.4 nm at 2 pulses/cycle to 28.0 nm at 4 pulses/cycle.

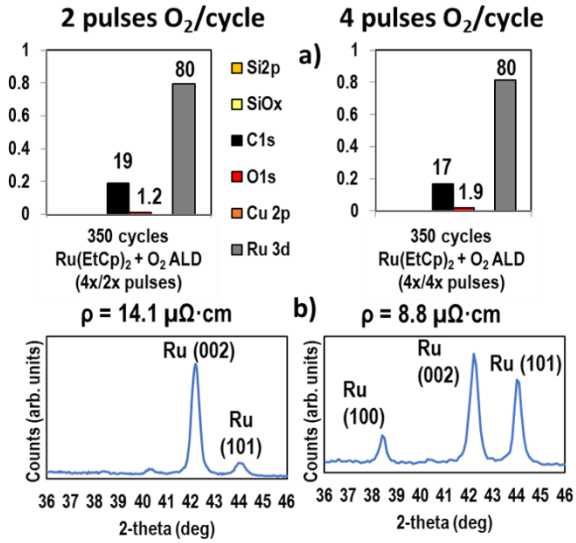

Fig. 4. Resistivity-oxygen dose relationship for Ru ALD using Ru(EtCp)$_2$. At 2 pulses/cycle, growth rate was 0.9 Å/cycle, while at 4 pulses/cycle, growth rate was 1.0 Å/cycle. a) Oxygen content of both films was sub 2%, with the 2 pulse and 4 pulse/cycle films having a resistivity of 14.1 and 8.8 μΩ·cm, respectively. b) XRD and XRR of the films show that the Ru(002) peak is dominant, but the Ru(101) grain size increases from 18.4 nm to 28.0 nm.

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