A Novel Thermally Stable Ruthenium Precursor Enabling Dense, Lower Resistivity and Inherent Selectivity against SiO_2 via Atomic Layer Deposition for Advanced Interconnects

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Ruthenium (Ru) has been widely investigated in the inteconnect metallization as a alternative candidate for replacing Copper (Cu), due to the reliability concerns of Cu such as electromigration (EM) resistance and time-dependent dielectric breakdown at especially scaled metal pitch. Ru is particularly promising due to its low resistivity with short electron mean free paths, high melting point, and chemical stability as a noble metal. It has high EM resistance inherently and does not require a diffusion barrier layer to prevent the diffusion into the surrounding dielectrics unlike Cu, making it suitable for advanced interconnect applications to overcome the miniaturization challenges. [1]
Atomic layer deposition (ALD) process can provide high-purity films with lower resistivity excellent step coverage in high-aspect-ratio structures and precise control over film thickness at the atomic scale due to its self-limiting surface reactions. ALD-Ru processes with O_2 as a co-reactant have been well examined and summarized with their various growth kinetics and thin film properties. The use of conventional high-valence precursors often suffers from a low growth per cycle (GPC). On the other hand, zero-valent Ru precursors also suffer from a relatively high resistivity mainly attributed to the poor thermal stability of the precursors (typically < 300 ^{o}C) to hinder a higher temperature deposition, although they show high GPCs and shorter incubation cycles. [2]
Since both high GPC with self-limiting behavior and better film quality are essential for the desired ALD process, we have developed a novel heteroleptic Ru precursor, which has two small and simple molecular structure ligands, trimethylenemethane (TMM) and isopropylmethylbenzene (*p*-cymene). This precursor, [Ru(TMM)(*p*-cymene), synthesized at TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan] shows a high thermal stability, no thermal self-decomposition up to 400 ^{o}C. Self-limiting growth behavior at 300 ^{o}C deposition was confirmed, corresponding to the excellent step coverage (>95%) on the trench wafer with aspect ratio ~4 (Figure.1). The GPC exhibits as high as 1.27 Å cycle^{-1} when using O_2 molecules as a reactant. Incubation periods on metallic substrates show relatively short (~8 cycles on TiN), while surprisingly extended incubation periods >1000 cycles were observed on SiO_2. It indicates that an inherent selective deposition made possible by this novel Ru precursor, facilitating the specific application of Ru interconnect metallization, for example, bottom-up metal filling in scaled vias. (Figure. 2)
The deposited film shows better qualities, large grain sizes and lower impurities by virtue of high process temperature, leading to lower resistivity as ~14.2 $\mu\Omega$ cm (300 ^{o}C, ~25 nm-thick Ru). The resistivity is still relatively maintained with the low value even at thinner thickness, being superior to the previously report about conventional Cu/TaN system for the reference [3] at < 10 nm when considering the thickness of diffusion barrier (TaN). Crystallographic analysis combined with Fuchs-Sondheimer-Mayadas-Shatzkes (FS-MS) modelling revealed that well enlarged crystallite and promoting the formation of coincidence site lattice (CSL), which is 3D superlattice facing two crystals with shared atoms to a specific orientation, are greatly attributed to mitigating grain boundary scattering, enabling as low as 10.6 $\mu\Omega$ cm (350 ^{o}C, ~34 nm-thick Ru) without post-annealing (Figure.3). These unique features and new findings using a novel Ru precursor will offer the further possibility of Ru metallization for advanced interconnects.

References

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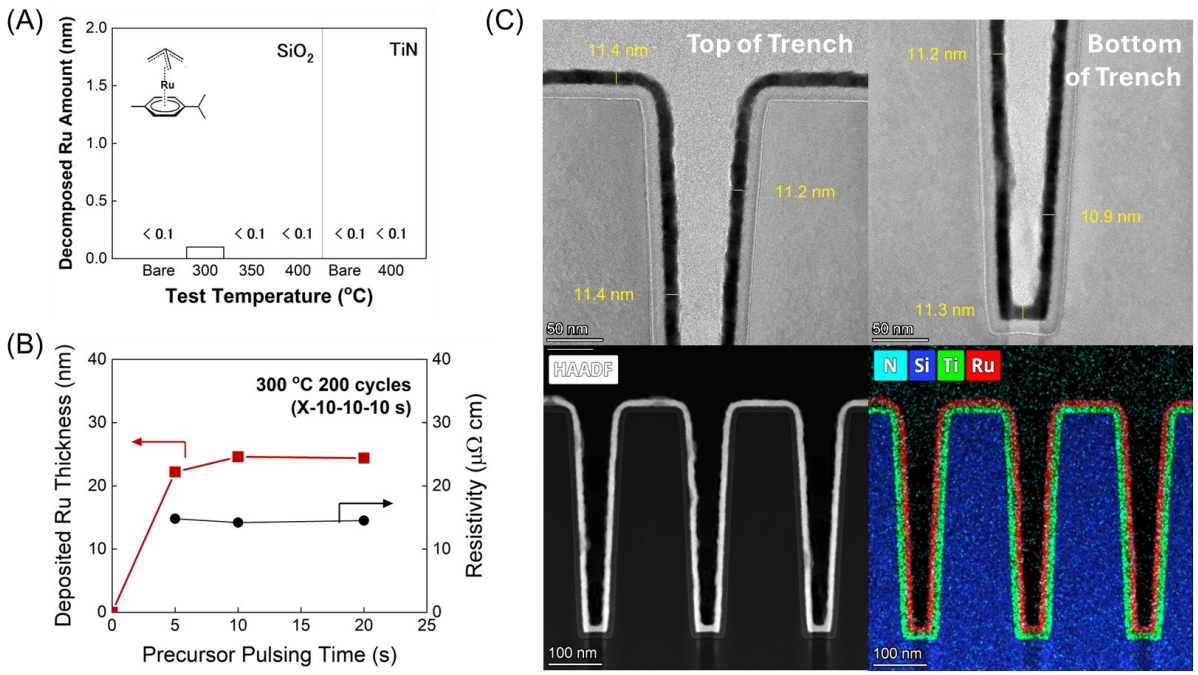

Figure 1. (A) Chemical structure of a novel Ru precursor [Ru(TMM)(*p*-cycme)] and its thermal stability evaluated by XRF where only the precursor was supplied into the ALD chamber without any reactants for 10 min. (B) Deposited Ru thickness by SEM and the resistivity of these thin films as a function of precursor pulsing time at 300 °C O_2 ALD with 200 cycles. (C) Cross-sectional TEM images at 300 °C deposition on TiN deposited trench wafer with aspect ratio ~4 (Top width: ~115 nm, Bottom width: 65 nm, Trench depth: ~415 nm), HAADF image (lower left) and elemental mapping quantification for full Ru, Ti, Si and N (lower right).

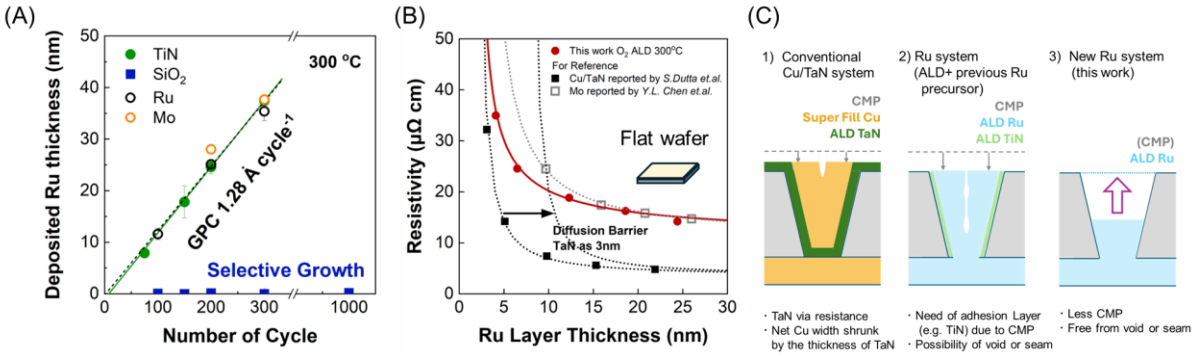

Figure 2. (A) The thickness of the ALD-Ru thin films deposited under optimized pulsing conditions as a function of the number of ALD cycles on TiN, SiO_2, Ru and Mo substrates. (B) Resistivity of deposited ALD-Ru and other metal (Cu, Mo; refs [3], [4]) thin films on flat wafer at 300 °C deposition (C) Schematic comparison images of via fabrication in the case of 1) conventional Cu/TaN system by superfilling technique for Cu and ALD for TaN, 2) Ru system by ALD using previous Ru precursor, 3) New Ru system by ALD using [Ru(TMM)(*p*-cymene)].

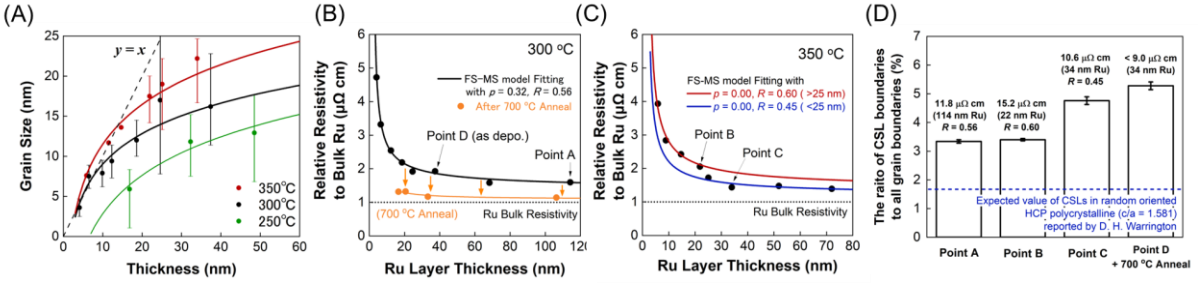

Figure 3. (A) Grain size derived from full width at half maximum of X-ray diffraction peaks using Scherrer formula at 250, 300, 350 °C. FS-MS modeling at a deposition temperature of (B) 300 °C, (C) 350 °C. (D) The relation between grain boundary scattering coefficient *R* and CSL ratio to all grain boundaries with ref [5].