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Ru ALD With Bulk-Like Resistivity for Interconnects

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***Abstract*—Ruthenium is viewed as a promising alternative to Cu and Co interconnect metals at M0/M1 interconnect layers due to its lower effective resistivity in highly-confined layers and vias, as well as its resistance to diffusion into porous low-k dielectrics and to electromigration. Atomic layer deposition of Ru has been reported with a variety of precursors, but the search for a Ru ALD process with a close-to-bulk (~7 μΩ·cm) resistivity is ongoing, with special interest in a process that can selectively-deposit low-resistance Ru films without passivants. In this work, Ru films with close-to-bulk resistivity deposited using $Ru(CpEt)_2$ were investigated using four-point-probe resistivity measurements, X-ray photoelectron spectroscopy (XPS) for chemical analysis, X-ray diffraction/reflectometry (XRD/XRR) for grain size and thicknesses, and scanning electron microscopy (SEM) and atomic force microscopy (AFM) for film morphology.**

Keywords—atomic layer deposition, ruthenium, interconnect metallization

I. Background and Experiment

Due to its low bulk resistivity and resistance to electromigration, Cu has been used as the interconnect metal of choice since the early 2000s [1]. However, as modern CMOS nodes continue to decrease pitch lengths and via widths decrease, the effective resistivity of Cu in the M0/M1 interconnect layers increases, motivating the use of alternate metals such as Co or Ru. Ru is of special interest owing to its short electron mean-free-path allowing for lower effective resistivity in narrow (<10nm) via widths compared to Co or Cu [2][3]. While many Ru ALD processes are available, the search for a low-resistivity Ru process is ongoing, with particular interest in a process that can selectively-deposit Ru films without the use of a passivant[4].

In this report, Ru ALD was performed using two processes, $Ru(CpEt)_2$ ("CpEt process", EMD Electronics) with O_2 as a co-reactant, and $Ru(DMBD)(CO)_3$ ("DMBD process", EMD Electronics) and tert-butyl amine (TBA) as coreactant. The CpEt process was performed at 300-360 °C deposition temperature at a pressure of ~1 Torr, while the DMBD process was performed at 160-180 °C at a pressure of ~1 Torr. Combinations of either or both processes were performed on SiO_2, HF-cleaned Si, low-k dielectric (SiCOH), Cu, and W substrates. Prior to deposition, samples were degreased with acetone, methanol, and DI water, followed by 30 minute ultra-high-vacuum anneal at 350 °C to remove atmospheric contaminants. After deposition, samples were transferred under vacuum to the attached UHV chamber for XPS (Scienta Omicron). Due to the overlap in binding energy between the C1s and Ru 3d XPS peaks, precise deconvolution of the two peaks is not possible and a rough quantitative estimate is given for the C content. 4-point-probe (Ossila Four-point-probe System, Ossila, Ltd.) measurements were performed after deposition was completed on films of dimensions 6 mm x 2 mm and a probe spacing of 1.27mm, corresponding to a geometric sheet resistance correction factor of 0.34 to account for the invalid semi-infinite approximation. XRD and XRR measurements were performed on the films to determine film thicknesses and grain sizes using the Scherrer approximation. After deposition, a forming gas anneal (FGA) at 450 °C was performed for 30 minutes to further reduce resistivity, and SEM and AFM used to inspect the morphology of the surface.

II. Low-resistivity Ru with $Ru(CpEt)_2 + O_2$

A study was performed using the cyclopentadienyl-based Ru precursor, $Ru(CpEt)_2$ with O_2 as a co-reactant. Fig. 1(a) shows XPS quantification of Ru ALD at 330 °C on SiO_2, Si, and low-k dielectric (SiCOH) substrates after 1000 cycles of Ru deposition. All three substrates were fully-attenuated in XPS, consistent with a continuous Ru film. On SiO_2, four-point-probe measurements resulted in a sheet resistance of 1.2 Ω/□. XRR measurements on SiO_2 resulted in a film thickness of 53 nm, resulting in a measured resistivity of 6.5 μΩ·cm, virtually equal to that of bulk Ru. Fig. 1(b) shows the XRD pattern of the Ru film deposited on SiO_2 with distinct Ru (100), (002), and (101) peaks, with grain sizes roughly 25 nm as calculated using the Scherrer approximation for grain size estimates. Fig. 1(c) shows an AFM image over a 2x2 μm region on the SiO_2 film showing a root-mean-square roughness of 2.4 nm, smooth compared with the thickness of the film.

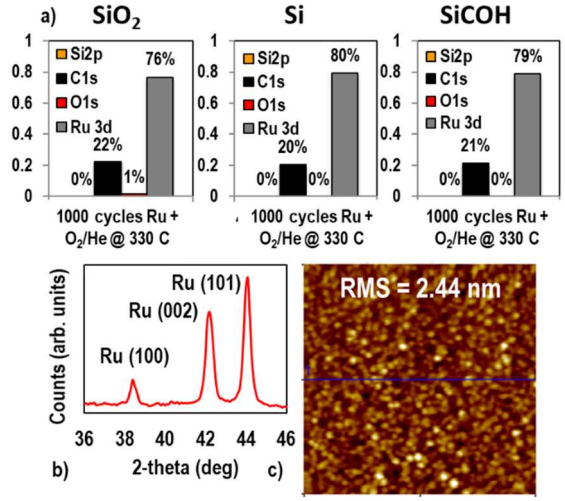

Fig. 1. XPS of Ru ALD at 330 °C with $Ru(CpEt)_2 + O_2$ on SiO_2/Si/SiCOH. (a) After 1000 cycles, all three substrates fully-attenuated on XPS with O below detection limit. (b) XRD shows distinct peaks for Ru (101), (002), and (100) orientations, with Scherrer approximations showing grain sizes of 25nm. (c) AFM shows film root-mean-square roughness of 2.4nm compared with a film thickness of 52 nm.

III. Low-temperature Ru with $Ru(DMBD)_2$ + TBA

The second process investigated was the DMBD process at 150 C. Fig. 2 shows XPS quantification for the deposition of Ru-DMBD at 150 C after the first 100 cycles and after an additional 400 cycles for a total of 500 cycles deposited. On SiO_2 and Cu, the substrate is nearly-fully attenuated at the first 100 cycles, while SiCOH has a substrate attenuation consistent with sub-monolayer (~0.2nm) coverage of Ru. After an additional 400 cycles, Cu and SiO_2 are fully buried, but some SiCOH substrate signal remains consistent with ~2nm film thickness.

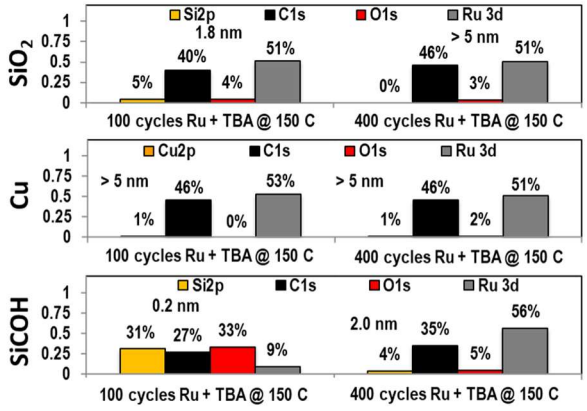

Fig. 2. XPS of Ru ALD at 150 °C with $Ru(DMBD)(CO)_3$ + TBA on SiO_2/Cu/SiCOH. After the first 100 cycles, SiO_2 and Cu are close to fully attenuated by the overlaying Ru film, while sub-monolayer coverage is present on SiCOH. After an additional 400 cycles, SiCOH is attenuated to ~2 nm Ru coverage while the other substrates are fully buried by the Ru film.

XRR measurement of the film deposited on SiO_2 shows a film thickness of 23nm and density of 7.3 g/cm^3, with a sheet resistance of 79 Ω/□ for a resistivity of ~180 μΩ·cm. XRD shows no clear grain orientation, consistent with the observed high level of C in the film and the measured high resistivity. A 450 C forming gas anneal was then performed for 30 minutes, after which a sheet resistance of 11 Ω/□ was measured. Thickness of the post-anneal film as measured by XRR was 12 nm and density of 11.9 g/cm^3, consistent with a resistivity of 12.5 μΩ·cm. XRD of the film then showed the presence of (002) and (101) grain orientations, with Scherrer-equation derived grain sizes of 11 and 12nm respectively.

IV. Substrate Comparison

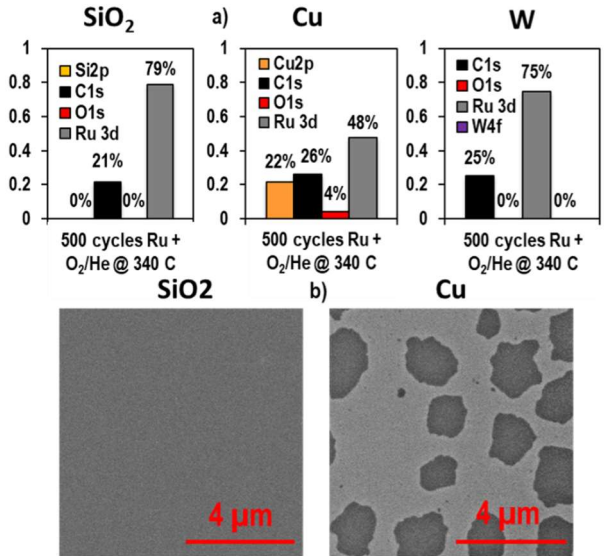

Fig. 3. XPS of Ru ALD at 340 °C with $Ru(CpEt)_2 + O_2$ on SiO_2/Cu/W. (a)XPS shows full attenuation of the substrates on SiO_2 and W samples, while only partial attenuation on the Cu sample. (b) SEM shows a smooth, uniform film on SiO_2 and W, while on W large voids are observed on the deposited Ru film consistent with the Cu signal observed by XPS.

As the intended purpose of Ru metallization is to serve as a low resistance via between interconnect layers, compatibility with other used metals is key. Fig. 3(a) demonstrates the deposition of the low-resistance Ru film using the CpEt process on SiO_2, Cu, and W substrates. After 500 cycles of Ru ALD at 340 C, the SiO_2 and W substrates were fully attenuated. However, the Cu substrate was only partially attenuated. On SiO_2, the Ru film thickness was 30 nm with a sheet resistance of 2.7 Ω/□, for a resistivity of 8.1 μΩ·cm. Fig. 3(b) shows SEM images of the film after deposition on SiO_2 and Cu. The films on SiO_2 and W were uniform and without major defects, while on Cu significant defects are observed. Comparison of this result with XPS is consistent with these defects being voids through which the underlying substrate is visible. This result can be explained by comparison of the surface free energies of Ru (3.0 J/m^2), Cu (1.8 J/m^2), and W (3.2 J/m^2), resulting in surface de-wetting of the Ru film on Cu during deposition [1][5]. During the low-temperature DMBD process, however, this de-wetting was not observed on the Cu substrate.

V. Bilayer Process

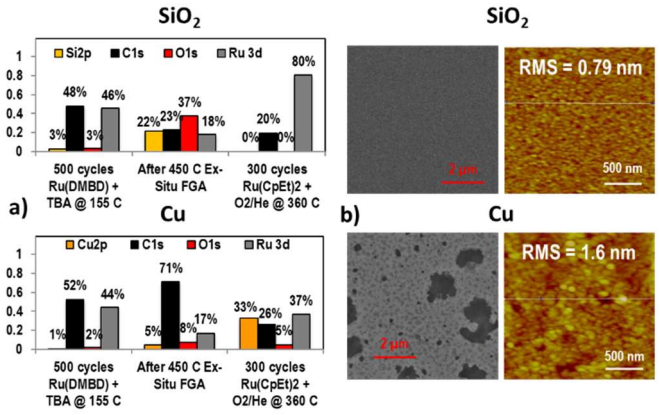

Fig. 4. XPS of Ru ALD using Ru-DMBD & Ru-CpEt Processes. (a) XPS of the DMBD process, followed by ex-situ FGA, then CpEt process on SiO_2 and Cu. (b) SEM over a 10x10 µm and AFM over a 2x2 µm area on SiO_2 and Cu after a second ex-situ FGA, showing void formation in the Ru film on Cu and a smooth film on SiO_2.

Due to the surface de-wetting issue, it was hypothesized that first depositing a sufficiently thick layer of Ru using the low-temperature Ru-DMBD process to act as a seed would allow for a continuous Ru film for the subsequent low-resistivity Ru-CpEt process. Fig. 4(a) illustrates the XPS data after 500 cycles of the Ru-DMBD process, an ex-situ 30 minute 450 C FGA, and the subsequent deposition of 300 cycles of Ru by the CpEt process on SiO_2 and Cu. After the DMBD process, both substrates are near-fully attenuated. After the FGA, both substrates are less attenuated before, with the additional carbon due to air exposure post-anneal. After 300 cycles of the CpEt process, the SiO_2 substrate is again fully attenuated, but the Cu remains visible.

After CpEt, the film thickness on SiO_2 was measured by XRR as 15.4 nm with a sheet resistivity of 6.5 Ω/□, corresponding to a film resistivity of 10 µΩ·cm, likely due to the higher resistivity of the DMBD-deposited Ru even after FGA. To further decrease the film resistivity, an additional 30 min 450 C FGA was performed, decreasing the film resistivity to 8.2 µΩ·cm. Fig. 4(b) shows both SEM images and AFM images of the film on SiO_2 and Cu, where a smooth continuous film of sub-nanometer roughness is observed on SiO_2. However, on Cu, the formation of voids in the film is again observed, with the addition of smaller pits likely due to the de-wetting of the film during the ex-situ FGA. AFM roughness of the Ru film on Cu is 2x that of the film on SiO_2 over a 2x2 µm region.

VI. Conclusion

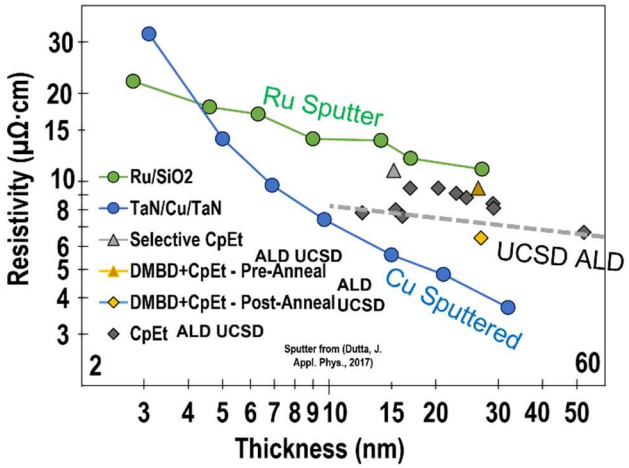

Fig. 5. Film thickness-resistivity relationship for films deposited via DC sputtering and ALD.

Fig. 5 compares the relationship between film resistivity and film thickness for a set of films deposited by sputter deposition by Dutta *et. al*, and Ru films deposited by ALD processes outlined in this report [6]. With optimized ALD conditions, these low-resistivity processes have the potential to allow for viable Ru films in barrierless via-fills as well as for the interconnect layers themselves at the M0/M1 level for metals with surface-free-energies close to that of the Ru such as W. However, further work remains to integrate the Ru films on top of existing Cu films without voids or impurities.

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