

Chemical selectivity and nucleation during ALD of Ru with the RuO₄ precursor

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Despite its higher bulk resistivity, ruthenium is proposed to replace copper in sub-10 nm interconnects, because it shows better electromigration behavior and doesn't need a barrier and liner. We developed thermal and plasma-enhanced ALD processes using RuO₄ and H₂ that allow for low-temperature deposition of high quality ruthenium thin films [1,2]. Here, we report on the inherent substrate selectivity for the thermal process on H-terminated Si (Si-H) versus SiO₂. *In situ* spectroscopic ellipsometry (SE) showed a growth delay of 60 cycles on SiO₂, while on Si-H growth occurred from the first cycle onward. Fig. 1 presents a cross-section high resolution TEM investigation of a Ru deposition on a patterned Si-H/SiO₂ substrate, revealing a smooth, continuous Ru film of 4.5 nm on the Si-H surface, with no growth on SiO₂. The chemical selectivity was further investigated in a vacuum cluster tool that allows for direct '*in vacuo*' sample transfer from the ALD setup to an XPS instrument. The strong oxidative nature of the RuO₄-precursor was confirmed to oxidize the Si-H surface, enabling Ru deposition, while no reaction can occur with SiO₂.

The nucleation on oxide substrates can be enhanced by switching from the thermal process to the plasma-enhanced ALD process [3]. However, *in situ* grazing incidence small angle X-ray scattering measurements at the synchrotron and *ex situ* SEM imaging revealed an island-like growth, which is to be avoided if continuous films and low film thicknesses are aimed for. An approach to enhance the nucleation of the RuO₄/H₂-gas process on oxide substrates was developed, based on exposing the surface to trimethylaluminum (TMA) just before the start of the ALD process. As confirmed by *in vacuo* XPS, the introduction of surface methyl groups during the TMA exposure makes the oxide surface reactive towards RuO₄, leading to immediate Ru deposition during the first ALD cycle. The swift nucleation resulted in films with a low roughness and sufficiently low resistivity value, comparable to the Ru thin films deposited on Si-H. Given the high reactivity of TMA, this approach presents a way to achieve Ru metallization of virtually any surface.

[1] M. M. Minjauw et al., J. Mater. Chem. C, 2015, 3, 132. [2] M. M. Minjauw et al., J. Mater. Chem. C, 2015, 3, 4848. [3] J. Dendooven et al., Rev. Sci. Instrum., 2016, 87, 113905.

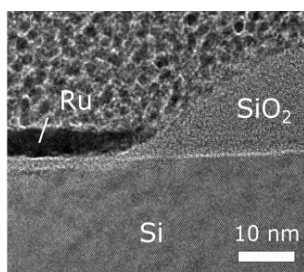


Figure 1 HR-TEM image of the Ru film selectively deposited on Si-H with no growth on SiO₂

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