

# Area Selective Atomic Layer Deposition of Molybdenum Films on Nanoscale Metal and Metal Nitride Patterns

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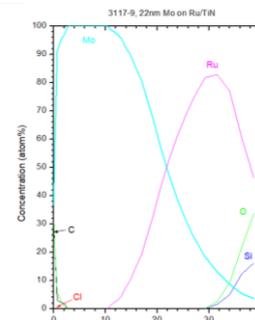
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## ABSTRACT

Deposition of conductive metal in super-narrow lines and vias represents significant challenge for scaling semiconductor devices. Cu interconnect lines show significant increase in resistivity below 10 nm and can't be used without a barrier due to electromigration. Tungsten inherently has higher resistivity compared to copper while precursor choice is often limited to tungsten hexafluoride which also requires a relatively thick barrier film to protect dielectric layer. Molybdenum (Mo) is considered as an attractive material for future devices. Mo has almost same level of low bulk resistivity comparing to W, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compared to W for films less than 10nm. While Mo films can be deposited by traditional CVD or ALD processes, area selective deposition of metal films can significantly reduce process steps and provide new options for device integration.

Here, we report area selective thermal ALD of Mo films on metal and metal nitride substrates using high purity molybdenum pentachloride ( $\text{MoCl}_5$ ) and molybdenum dichloride dioxide ( $\text{MoO}_2\text{Cl}_2$ ). Deposition of Mo films was investigated by thermal ALD process with hydrogen reactant gas at 350-500°C on various substrates, such as aluminum oxide, silicon oxide, titanium nitride and ruthenium metal. Both Mo precursors showed higher deposition rate on TiN substrate compared to  $\text{SiO}_2$ . However,  $\text{MoCl}_5$  showed significantly higher process selectivity toward TiN and Ru. The dependence of selectivity on process conditions, such as precursor ampoule temperature, chamber pressure and deposition temperature was investigated. Higher selectivity was attributed to  $\text{MoCl}_5$  ability to self-etch deposited Mo film. The films were characterized by XRF, 4-point probe, XPS, SIMS and XRD. Molybdenum films deposited from  $\text{MoCl}_5$  on Ru substrate at 450°C showed no detectable chloride by XPS and  $\ll 0.01$  at % by SIMS.

High resolution TEM of Mo films on patterned TiN/ $\text{SiO}_2$  and Ru/LowK wafers shows a seamless bottom-up molybdenum fill on highly challenging structures with CD < 30 nm and feature height > 80 nm, with very minor defects on  $\text{SiO}_2$  and LowK dielectric. Over 10 times enhancement of effective deposition rate was observed inside the features compared to blanket film. For example, selected process conditions provided 4.2 nm Mo film on blanket Ru film while the same conditions deposited over 80 nm Mo film inside of ~ 20 nm via. The result may suggest that ASD mechanism on nanoscale is different from the macroscale mechanism.



XPS of Mo film on Ru blanket