In-Situ Ellipsometric Study of the Adsorption of Additives on Ruthenium

Copper (Cu) is the material of choice for on-chip interconnects metallization of semiconductor devices due to its low electrical resistivity. However, Cu can quickly diffuse through and poison the active and passive regions of Si devices. It is therefore necessary to line Cu interconnects with barrier materials such as tantalum (Ta) or titanium nitride (TiN) which are resistant to Cu interdiffusion. These current barrier materials have high electrical resistance and require a vapor-deposited Cu seed layer to promote Cu metallization. Ruthenium (Ru) is a material with significant resistance to Cu intermixing and a lower electrical resistivity than Ta or TiN. In addition, Cu can be directly electroplated onto Ru without the need for first depositing a seed layer. These attributes make Ru a possible candidate for the next generation barrier or liner material.

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Copper (Cu) interconnects are currently fabricated by an electroplating process. Certain additives, such as polyethylene glycol (PEG) and chloride ion (Cl^-) are used in trace amounts in the plating bath to selectively control the rate of Cu deposition to provide defect-free superconformal filling of the interconnect trenches and vias. NIST has previously used in-situ spectroscopic ellipsometry (SE) to characterize the development of the Cl^--induced PEG inhibiting layer on Cu surfaces that is an essential step in the superconformal filling process. In the current work, SE was applied to the study of the Ru surface, and the interaction of Cu, Cl^-, and PEG on Ru, to understand the implications of the introduction of a new material (Ru) to the established superconformal plating process.

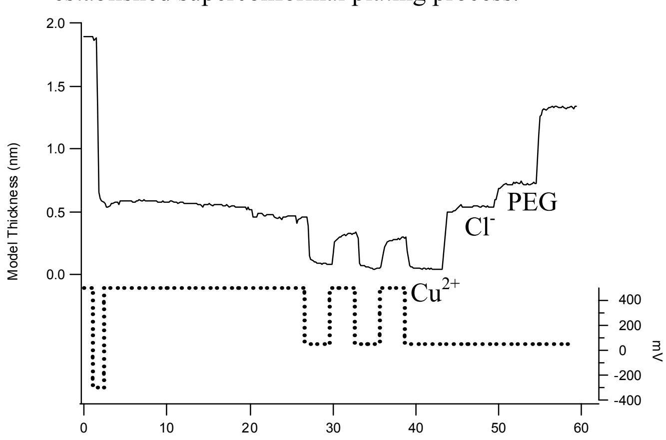

Figure 1:The model thickness (solid line) of an activated Ru surface in which a Cu under potential deposition (upd) layer was formed subsequent to Cu^{2+} addition (43 min), followed by the addition of Cl^- (49 min) and PEG (54 min), with all additions made at 0.050 V. The history of the applied potential is given by the dotted line

It is well established that the native oxide present on Ru is deleterious to both Cu adhesion and superconformal filling. In Figure 1 shows SE data from an "as received" Ru sample. The activation of the surface by reduction at negative potentials of –0.30 V is shown. It was determined that a thin (≈ monolayer) of oxide is re-established at slightly positive potentials, which can be reversibly removed and re-grown by cycling between +0.50 V and +0.05 V (features between 20 min and 40 min). Upon the introduction of Cu ions at a potential of + 0.05 V, Cu under potential deposition (upd: deposition of a monolayer of Cu at potentials positive of those required for steady state plating) occurs. On the Cu upd layer, both Cl^- and PEG adsorb in a fashion similar to their adsorption on bulk Cu (steps near 50 min and 60 min). In Figure 2 it is shown that this Cl^-/PEG film on the Cu upd layer inhibits subsequent Cu plating. This observation is critical, as the initial inhibition of Cu plating is an essential step in the superconformal filling process.

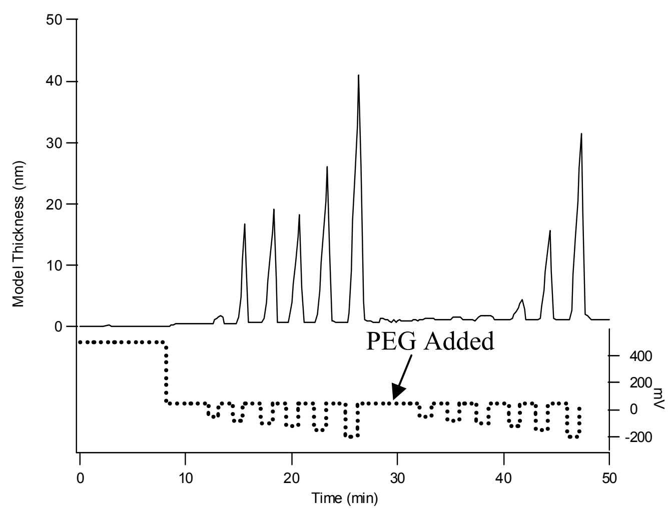

Figure 2: The model thickness (solid line) of an activated Ru surface in which a Cu upd layer was formed subsequent to Cu^{2+} addition at 0.050 V. Chloride is present in the electrolyte. The potential (dotted line) was stepped to increasingly negative potentials for 1 min intervals, resulting in bulk metal deposition, and then stepped back to 0.050 V. PEG was added at 28 min, and the potential steps repeated. Clear inhibition of Cu electrodeposition is demonstrated relevant to potentials where plating was previously observed.

Impact: These results provide some understanding of the mechanism by which Cu can be electrodeposited on Ru, which may have applications as a next-generation barrier material in semiconductor fabrication. Importantly, the Cl^-

and PEG additive chemistry on the Cu upd layer is similar to that on bulk Cu and supports superconformal filling.

Future Plans:

SPS and MPS are plating bath components that serve as activators for Cu electrodeposition. Studies of the three-component PEG/Cl^-/SPS and PEG/Cl^-/MPS system are underway to investigate the dynamics of the bis-(3-sodiumsulfopropyl disulfide) (SPS) or (3-mercaptopropyl) sulfonate (MPS) displacement of the inhibitory PEG layer formed on Cu substrates in the presence of Cl^- at various relevant plating potentials.

Publications:

M.L. Walker, L.J. Richter, D. Josell, and T.P. Moffat**,** **"An In-Situ Ellipsometric Study of Cl^--Induced Adsorption of PEG on Ru and on Underpotential Deposited Cu on Ru"**, *J. Electrochem. Soc.* **153**, C235 (2006).

T.P. Moffat, M.L. Walker, P.J. Chen, J.E. Bonevich, W.F. Egelhoff , L.J. Richter, D. Josell, C. Witt, T. Aaltonen, M. Ritala, and M. Leskelä, **"Electrodeposition of Cu on Ru Barrier Layers for Damascene Processing"**, *J. Electrochem. Soc.* **153,** C37 (2006).