

I. Deliverable:

Name: Report on the identification of potential ECMP baths for Ru and Ta: Initial estimates of Barrier/Cu selectivity

Task ID: 425.016

Task Title: EHS Impact of Electrochemical Planarization Technologies

II. Abstract:

With reduction in node size, a need exists for the development of direct deposition methods, in which Cu is electrodeposited directly onto barrier without use of a seed layer. This may require the introduction of ruthenium, to be used with Ta-based materials. In consultation with other PI, we have focused our efforts on understanding the electrochemical oxidation of ruthenium in phosphate-based electrolytes. Such electrolytes also show promise for Cu-ECMP. The effect of benzotriazole (BTA) and ceric ammonia nitrate (CAN) are shown to have an impact on the polarization behavior. In particular BTA decreases Ru oxidation rates, similar to the effect seen on Cu, which could be interesting for the optimization of polishing techniques for Cu and Ru. Results show a comparative analysis of current between Ru/Cu in a potential range of -1 to 0.8 V, which may not directly relate to specificity.

III. Technical Results:

To investigate Cu/Ru selectivity, electrochemical experiments were conducted using a square piece of ruthenium foil (6mm x 6mm) with a thickness of 1 mm and a purity of 99.9% and a Cu RDE. The area of Ru typically used during electrochemical experiments was 0.06 cm²; while the RDE had an area of 0.196 cm². Each sample was immersed in an electrolyte contained in a glass beaker with no flow present and the working electrode was stationary. A silver/silver chloride (Ag/AgCl) reference electrode and a platinum (Pt) wire counter electrode were also present in the electrolyte. Removal rates were calculated theoretically, assuming the validity of Faraday's law, and assuming that four electrons are being transferred in ruthenium's case and two for the case of copper.

Figure 1 illustrates the effect of potential on the removal rate of ruthenium in different electrolytes. Similar to the effect that BTA has on copper, it can be seen that at low potentials (<1 V), BTA slightly inhibits Ru removal. Therefore, there is potential overlap between a polishing process for both Cu and Ru. The addition of CAN did not enhance removal rate of ruthenium in pure phosphoric acid. When CAN was added to the electrolyte containing 1 M potassium phosphate with a pH value of 2, a cloud-like sediment formed with a whitish green color. Therefore, due to the instability of this combination, further removal studies were not performed with CAN at a pH value of 2.

Figure 2 shows the ratio of current of Ru compared to Cu using various electrolytes at two different operating potentials, 0.5 and 0.8 V. These results suggest that in a potassium phosphate based electrolyte containing BTA could be least preferential to Ru etching. This corresponds to the fact that BTA is slightly inhibiting the dissolution of Ru in that potential region. This indicates that potassium phosphate based electrolytes should potentially be considered for polishing Ru. Currently we are exploring other potential pH values using a potassium phosphate electrolyte, as well as other oxidizers to enhance removal rate such as mono/dipersulfates (S₂O₈²⁻) and persulfuric acid, due to the instability of CAN in this electrolyte.

Figure 1: Theoretical removal rates of Ru in nm s^{-1} in (A) 1 M pH 2, (B) 1 M pH 2 + 0.001 M BTA, (C) Phosphoric Acid, (D) Phosphoric Acid + 0.01 M CAN.

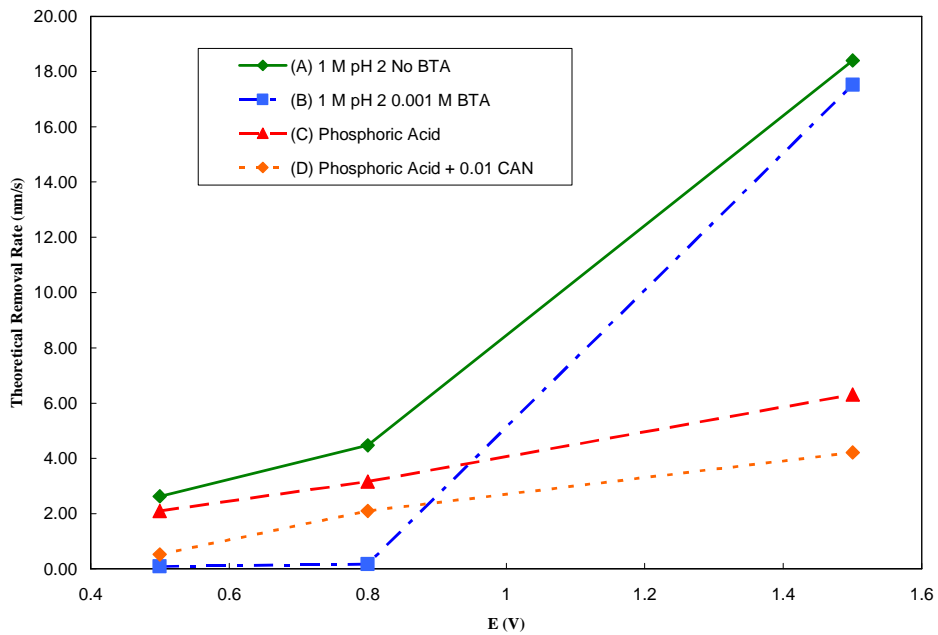


Figure 2: Ratio of current between Ru/Cu at two applied potentials in electrolytes composed of : (A) 1 M pH 2, (B) 1 M pH 2 + 0.001 M BTA, (C) Phosphoric Acid, (D) Phosphoric Acid + 0.01 M CAN

