I. Deliverable:

Name: Identification of Bath Chemistries for Ru: Electrochemical Characterization Results
Task ID: 425.016
Task Title: EHS Impact of Electrochemical Planarization Technologies
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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 show 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.

III. Technical Results:

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%. The area typically used during electrochemical experiments is 6 mm^2; other regions of the sample were protected with kapton tape. The 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.

Figure 1 shows the open circuit potential (OCP) of electrolytes currently being used in preliminary investigations. The OCP was monitored for three minutes for all solutions shown. It can be seen from Figure 1 that the addition of CAN to concentrated phosphoric acid dramatically increased the OCP from 0.27 V to 0.88 V respectively. In a phosphate based electrolyte at a pH value of approximately 2, the addition of the inhibitor, BTA, also increased the OCP from a value of 0.035 V to 0.31 V.

Figure 2 shows anodic polarization curves performed with a scan rate of 10 mV s^{-1} of various electrolytes. These scans were performed from -1.5 to 2 V shown on the x axis and the log of current density on the y axis. Immediately after starting the scan, bubbles formed on the working electrode attributed to hydrogen evolution in the negative potential region. From 0 to 1.0 V, in all cases, a black film formed on the working electrode, which we assumed to be an oxide of ruthenium, specifically ruthenium (IV) oxide (RuO_2). However, in phosphoric acid, the black film was easily washed off the surface using DI water post electrochemical treatment; in all other electrolytes the film remained intact after rinsing with DI water. In all cases after 1.0 V, oxygen evolution occurred which accounts for the increase in current densities.   It can be seen that the corrosion potential, E_{corr}, when CAN is present in phosphoric acid is much higher than in pure phosphoric acid. Assuming the validity of Faraday's law, and assuming that four electrons are being transferred, removal rates in nm s^{-1} at 0.8 V can be estimated as: A) 0.11 B) 0.44 C) 0.15 D) 3.05 E) 0.21.   In a potassium based electrolyte containing no BTA, a removal rate of approximately 3 nm s^{-1} can be achieved. Adding BTA to the electrolyte significantly decreases the removal of Ru to 0.21 nm s^{-1}. This indicates that potassium phosphate based electrolytes could potentially be considered for polishing Ru.

Figure 1: Open Circuit Potential (OCP) measurements using Ru as the working electrode in: A) concentrated phosphoric acid + 0.01 M CAN, B) DI water + 0.01 M CAN, C) concentrated phosphoric acid, D) 1 M potassium phosphate with a pH value of 2, E) 1 M potassium phosphate with a pH value of 2 + 0.001 M BTA
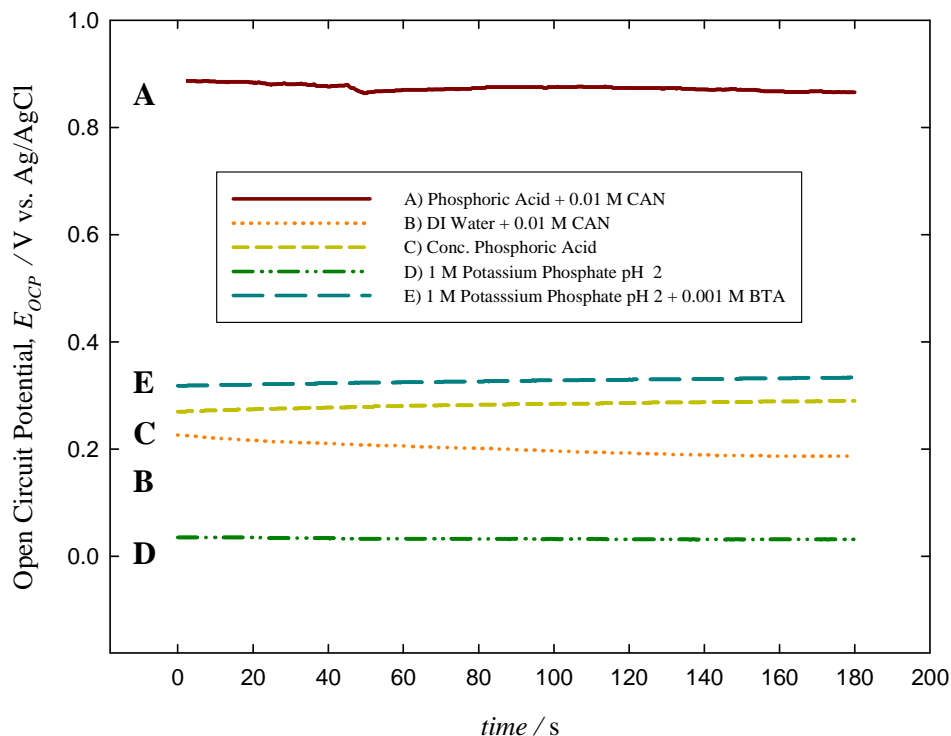

Figure 2: Potentiodynamic polarization curves of Ru foil scanned from -1.5 to 2 V with a scan rate of 10 mV s^{-1} in: A) concentrated phosphoric acid + 0.01 M CAN, B) DI water + 0.01 M CAN, C) concentrated phosphoric acid, D) 1 M potassium phosphate with a pH value of 2, E) 1 M potassium phosphate with a pH value of 2 + 0.001 M BTA