Task ID: 425.022
Task Title: Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro- and Nano-Electronics Manufacturing
Deliverable: Report on the completion of comprehensive cleaning model development in subtask 3, ready for both process and ESH assessment of proposed cleaning methods and procedures

Abstract:

Back End of Line cleaning of copper damascene structures requires chemical formulations that can selectively remove post etch residue, without etching the sidewall dielectric and underlying copper lines. A significant portion of the PER include copper oxides, which need to be removed from narrow, high aspect ratio features. Many of the commercially available formulations such as semi aqueous fluoride (SAF) chemical systems contain organic solvents to minimize the dielectric loss as well as to facilitate solution penetration into the residue films. However, the need for developing environmentally benign formulations has necessitated reduction in solvent levels. Further, there are also no cleaning end point detection techniques currently in place, which could be useful in controlling process times as well as minimizing critical dimension loss and copper corrosion.

Technical Results and Data:

The usefulness of semi aqueous fluoride formulations having *low solvent* content, in selectively removing controlled thicknesses of copper oxide films, over copper and TEOS has been studied. Dimethyl Sulfoxide (DMSO) has been used as the solvent and Ammonium Fluoride (NH_4F) has been used as the fluoride source. Systematic evaluation of solution variables, namely DMSO and NH_4F concentrations as well as pH has led to the development of an optimized formulation containing 29% DMSO, 1% NH_4F (pH 4), which has a CuO_X /Cu selectivity of ~130:1 and CuO_X/TEOS selectivity of ~10:1. It has been shown that a small amount (~29%) of solvent is necessary for obtaining reasonable selectivity over TEOS.

In the second part of the study, a cleaning end point detection technique based on electrochemical impedance spectroscopy has been developed. Controlled thicknesses of copper oxides thermally grown on copper have been used as model films to demonstrate the technique. Impedance spectra of copper oxide films have been measured as a function of immersion time in various formulations and the data has been analyzed using equivalent circuit models. Values of circuit parameters have been extracted to detect the completion of copper oxide film removal and transition to copper surface. Circuit parameters of interest include the capacitance (C_{oxide}) and resistance (R_{oxide}) of the passive copper oxide film, which change continuously as the film dissolves in the solution. As the film thickness is reduced, C_{oxide} typically increases and R_{oxide} decreases, since capacitance is inversely proportional to thickness of the oxide, whereas resistance is directly proportional to oxide thickness. At the end point, C_{oxide} becomes very large and R_{oxide} becomes very small. Beyond the end point, C_{oxide} starts decreasing slightly and R_{oxide} increases slightly due to repassivation/corrosion of the surface. Therefore, by

detecting the time corresponding to the maximum in C_{oxide} and minimum in $R_{oxide,}$ the dissolution end point is determined. Using a similar methodology, the electrochemical impedance spectroscopy technique is being extended to the determination of cleaning end point in patterned test structures containing residues. The technique can also be used as a method for rapid evaluation of cleaning formulations.