546d Copper Chelation for Microelectronic Interconnects in Supercritical Carbon Dioxide

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Carbon dioxide is an environmentally benign solvent with high surface wetting properties, tunability, recyclability and low viscosity. With these potential advantages, condensed and/or supercritical (sc) CO2 has the potential to replace the aqueous chemical mechanical planarization processes used in the microelectronics industry to form multi-layer interconnects from porous low κ inorganic and organic interlayer dielectrics. We have studied the use of organic peroxides and various ligand families as oxidants and chelants for copper in sc CO2. Copper chelation kinetics and surface composition analyses will be discussed along with results from electrochemical measurements made in aqueous and low dielectric strength media.

In order to obtain a fundamental understanding of the CMP process in “dry” solvents such as CO2, we have first investigated the chemical aspects of etching copper metal in aqueous and low dielectric strength media. The current study compares several -diketones, dithiocarbamates,βchelant families (bisacetylacetonate(ethylenediamine)). The amount of copper removed was obtained by measuring the weight loss and surface analysis studies include results from atomic force microscopy and x-ray photoelectron spectroscopy.

Mechanistic and kinetic studies were performed using a variety of copper starting materials in order to determine the effect of surface speciation on copper removal. The copper materials were added to 10 mL of hexanes containing either ligand and/or ligand and oxidant and allowed to react for up to 24 hours. The reaction rate of the complexes with ligand and oxidant increased in the order: CuSO4•5H2O < copper coupon << CuO < Cu(OH)2 < CuF2 << Cu2O. After characterizing reactions in hexanes, supercritical carbon dioxide was used and rates of removal of copper were found to be superior than in traditional solvents. Global rate expressions as well as mechanistically derived rate expressions were developed and important parameters identified.