546e Copper Etching Using Hexafluoroacetylacetone (Hfach) Dissolved in Supercritical Co_2: a Kinetic Investigation

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Supercritical carbon dioxide ($scCO_2$) has a unique set of physical properties making it a useful solvent in a variety of industries, including microelectronics where it has been used to deposit, etch, and clean thin insulator and metal films. A low surface tension and high diffusivity are advantageous for developing high throughput processes in confined geometries, such as porous structures and high aspect ratio vias. Accessible critical pressure and temperature values, nontoxicity, and tunable density make CO_2 an attractive solvent for a wide range of industrial processes. Whereas significant efforts have been made to explain the kinetics and mechanisms involved in supercritical fluid deposition (SFD) of metallic films,[1] supercritical fluid etching (SFE) of metals has only been demonstrated on blanket metal films without a comprehensive explanation of the reaction kinetics and mechanism.[2] Because $scCO_2$ is a non-polar, aprotic solvent, etching of metallic films requires the preparation of chemical formulations in the dense fluid to solvate ionic etching products. This study focuses on the kinetics of supercritical fluid etching of Cu metal films using the chelator hexafluoroacetylacetone (hfacH) dissolved in $scCO_2$. The fluorinated variant of the acetylacetone ligand was chosen because of its solubility in $scCO_2$ and its demonstrated capacity for copper chelation and product solvation in $scCO_2$. Etching using hfacH is isotropic and depends on the oxidation state and structure of the copper film. In a two-step process consisting of copper oxidation followed by etching using hfacH in $scCO_2$ mixtures, the kinetics of copper etching were measured as a function of temperature, pressure, and hfacH concentration. Copper metal films were covered with a thin cupric oxide layer with a flake-like morphology through oxidation in aqueous hydrogen peroxide solution. Using a recirculating batch reactor system designed to provide extremely precise control of temperature, pressure, and exposure time, etching rates were measured as a function of these parameters. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to characterize the surface and composition of the copper films before and after etching in $scCO_2$. Operating temperatures varied between 55 and 85°C (± 1°C) at a pressure of 185 bar (± 2 bar) with hfacH concentrations ranging from 1000 to 5000 ppm. A rate law for the process of copper etching using hfacH in $scCO_2$ was developed based on an apparent activation energy of 64.4 (± 6.8) kJ/mol (95% C.I.) obtained from an Arrhenius analysis. Mechanistic aspects of the etching process were modeled similar to a heterogeneous catalytic surface reaction, considering the effects of metallic surface morphology and surface concentration and binding of hfacH molecules. These results serve to help fundamentally characterize the mechanistic and kinetic steps involved in SFE of metal films.

1. Zong, Y., Watkins, J.J. Deposition of Copper by the H2-Assisted Reduction in Supercritical Carbon Dioxide: Kinetics and Reaction Mechanism. *Chem. Mat.* **2005**, 17, 560.

2. Xie. B., Finstad, C., Muscat, A.J. Removal of Copper from Silicon Surfaces Using Hexafluoroacetylacetone (hfacH) Dissolved in Supercritical Carbon Dioxide. *Chem. Mat.* **2005**, 17, 1753.