546b Reductive Deposition of Cerium Oxide Films in Carbon Dioxide

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Cerium oxides have received much attention in recent years due to their ability to reversibly transform between their cerous (III) and ceric (IV) forms depending on the environment. This enables use as a membrane system for oxygen transport, which has lead to a number of applications in catalysis and solid oxide fuel cells. Here we investigate a novel deposition scheme that involves the growth of metal oxide films in supercritical carbon dioxide using a cold-wall reactor.

The deposition of metal films in supercritical fluids is well established. The technique is analogous to CVD but carried out in a pressurized supercritical carbon dioxide medium allowing for orders of magnitude greater concentrations of deposition precursor to be solubilized by the fluid. In many cases the deposition is reaction rate limited over all available surfaces, resulting in even coverage of high aspect ratio structures. The unique properties of supercritical fluids also offer the benefit of zero surface tension and consequentially pose no danger of capillary damage to any substrate features. Depositions are carried out in a hydrogen environment and yield films with excellent purity, typically at lower temperatures than the equivalent CVD process.

Our current investigation involves the deposition of cerium oxide using tetrakis(2,2,6,6-tetramethyl heptane-3,5-dionato) as the precursor, yielding 80 -300 nm thick films on silicon test wafers. Depositions occur in the presence of water and a reducing agent at temperatures of 200 – 300 °C to yield high quality planar films. The deposition proceeds in the absence of an additional oxygen source. Film thickness can be controlled by varying the substrate temperature and deposition time. XPS analysis shows a mixture of CeO2 and Ce2O3 on removal of the substrate from the deposition reactor. The films can then be annealed to produce a single oxide product. The films are well adhered and free of carbon contamination.

Current studies have examined deposition of pure cerium oxide films, while future work will focus on mixed oxide films.