TECH HIGHLIGHTS

Electrodeposition of Epitaxial ZnSe on InP

Zinc selenide, a semiconductor material with a direct optical transition and a high bandgap value, has potential applications in optoelectronic devices such as light emitting diodes and solar cells. Thin films of ZnSe are typically prepared by vacuum evaporation, chemical vapor deposition, sputtering, or spray pyrolysis. A collaborative research team from the Ecole Nationale Superieure de Chimie de Paris, the Universite Pierre et Marie Curie in Paris, and the Universidad Catolica de Valparaiso in Chile have described a simple, low cost, low temperature method for deposition of epitaxial ZnSe films on InP substrates. They performed controlled-potential electrodeposition at 150°C from a dimethylsulfoxide (DMSO) electrolyte containing 0.1 M $ZnCl_2$, 0.1 M LiCl, and saturated elemental Se. SEM analysis revealed that deposition at potentials more negative than –1.4 V (*vs.* mercury/mercurous sulfate) produces fully dense, homogeneous, stoichiometric ZnSe films. High-energy electron diffraction experiments showed that the films are single crystal and epitaxial. Optical transmission measurements reveal a direct absorption transition with a 2.64 bandgap, in agreement with literature values for single crystal ZnSe. This is the first report of epitaxial electrodeposition of ZnSe from DMSO, and the authors delineate the improved characteristics of these films compared to those produced by electrodeposition from aqueous acids (which result in an excess of Se) and by controlled-current electrodeposition from DMSO (which results in ZnSe nanocrystals).

*From: Electrochem. Solid-State Lett., **7** (6), C75 (2004)*

Enhancement of CO Tolerance of Pt Catalysts

Tolerance to small amounts of CO is important for proton exchange membrane fuel cells (PEMFCs) operating on hydrogen obtained from reforming of carbon-based fuels. Pt-based catalysts used today suffer high anode polarization losses due to CO poisoning. Researchers at Fuel Cell Energy, Inc. and the University of Connecticut recently reported two approaches to enhancing the CO tolerance of Pt catalysts. The first strategy involves the use of metal macrocycle complexes as co-catalysts with platinum. These complexes are believed to act as redox mediators that can oxidize CO at potentials lower than Pt, thus reducing the anode polarization for oxidation of H_2. In particular, a 40% reduction was achieved with a Mo-porphyrin complex in a fuel containing 104 ppm CO. In the second approach, sulfur-containing Pt catalysts were synthesized using $Na_2S_2O_3$ as the reducing agent. These catalysts showed not only inhibition for CO adsorption, but low polarization for hydrogen oxidation as well. The lowest anode polarization for oxidation of H_2 containing 104 ppm CO obtained in the study was 0.167 V at 400 mA/cm^2, which is lower than that for the widely used Pt-Ru catalyst.

*From: J. Electrochem. Soc., **151** (5), A703 and A710 (2004)*

Plating of Copper in Deep Submicrometer Holes

Copper electrodeposition is widely used in the semiconductor industry for the fabrication of interconnects in ultralarge scale integrated circuits (ULSIs). The typical process involves plating over a sputtered copper seed layer. However, as the dimensions of state-of-the-art interconnects are decreased, it becomes increasingly difficult to prepare a continuous seed layer. This can result in void formation during subsequent Cu electrodeposition. Scientists at Hiroshima University in Japan have shown that electroless deposition can provide a viable alternative for achieving void-free filling in deep submicrometer holes. The authors studied a number of inhibitors and found that sulfopropyl-sulfonate (SPS) was effective in achieving bottom-up deposition over a Pd catalyst layer deposited using ion cluster beam deposition. Tracking the ratio of the thickness of copper at the bottom of the trench to that at the top (termed bottom-up ratio), they showed that the ratio increases as SPS concentration increases until a point where inhibition results in no deposition. In addition, this ratio decreases as the hole diameter increases. The authors explained the results by suggesting that the inhibitor undergoes diffusion-controlled adsorption. Since inhibitor diffusion is relatively low at the bottom of the trench, copper deposition is enhanced. The result is bottom-up filling of copper in these deep submicrometer holes.

*From: Electrochem. Solid-State Lett., **7** (6), C78 (2004)*

Back Side Damage Gettering of Copper in Silicon

Contamination of semiconductor silicon by trace metal impurities can degrade integrated circuit performance by reducing carrier lifetimes, increasing reverse-bias junction leakage currents, or degrading the dielectric breakdown strength of silicon dioxide layers. Since silicon wafers are inevitably contaminated during device processing, gettering techniques that remove unwanted impurities from active device regions are essential. In one approach, the polished front side of the wafer is protected from contamination by the intentional introduction of crystal defects in the back side that serve as gettering sites. Researchers at Tohoku University in Japan recently reported a novel technique for introducing back side damage based on the impact force produced by the collapse of cavitation bubbles. In their experiment, wafer back sides were first treated in a water-cavitating jet apparatus. The wafers were then intentionally contaminated with copper and oxidized in humid O_2 at 1100°C (to diffuse the Cu from the wafer surface to the gettering sites). A Secco decoration etchant revealed that contamination was eliminated from the front surface in regions aligned with areas where back side damage had been introduced. In contrast, wafer front regions that were not aligned with back side damage regions exhibited etch pits characteristic of oxidation-induced stacking faults. The authors propose that this gettering approach is cleaner and simpler than ion implantation, mechanical grinding, shot blasting, or laser treatment techniques.

*From: Electrochem. Solid-State Lett., **7** (4), G51 (2004)*

A New Model for Dendritic Growth

Dendrite formation, a primary failure mechanism in lithium/polymer batteries, is typically divided into two regimes: initiation and propagation. Since theoretical studies suggest that dendrite growth cannot be prevented once a system has reached the propagation regime, analysis of initiation phenomena is the only route to identify conditions that prevent dendrite formation. Monroe and Newman at the University of California, Berkeley, have developed a new kinetic model that describes cathodic roughening and dendritic growth. They extended the kinetic expressions employed in Mullins-Sekerka linear stability theory and the Barton-Bockris dendrite-propagation model (both of which contain the effects of surface tension and local concentration deviations induced by surface roughening) to include mechanical forces such as elasticity, viscous drag, and pressure. The authors demonstrate the effects of these parameters on exchange current densities and potentials at roughening interfaces. Both of the earlier theories can be derived as special cases of the new model, thereby validating the proposed model and elucidating the fundamental assumptions on which the two previous theories rely. Future work will extend the model to the lithium/polymer system and will incorporate linear elasticity theory to demonstrate how the elastic moduli of the polymer and lithium contribute to evolving surface morphology during polarization.

*From: J. Electrochem. Soc., **151** (6), A880 (2004)*

Tech Highlights was prepared by Zenghe Liu of Abbott Diabetes Care, Venkat Srinivasan of Lawrence Berkeley National Laboratory, and Mike Kelly of Sandia National Laboratories.