

Electroless Deposition of Co-P and Co-W-P Alloys

The electroless deposition of cobalt alloys is being widely studied for use in integrated circuit (IC) and microelectromechanical system (MEMS) applications. For example, thin films of Co-W-P alloys are effective as high-temperature (up to 550°C) barrier and cladding layers for copper interconnections produced by the dual damascene process. These thin films protect Cu metallization from corrosion, prevent Cu diffusion into silicon device regions, and promote good adhesion between Cu and dielectric layers. Researchers at Mattson Technology in California and Tel-Aviv University in Israel have reported an electrochemical study of the electroless deposition of Co-P and Co-W-P alloys from sulfate baths containing a hypophosphite reducing agent and a citrate complexing agent. Experimental results (polarization experiments on Co-P and Co-W-P working electrodes, in situ measurements of electroless deposition mixed potentials, gravimetric determinations of deposition rates, and X-ray photoelectron spectroscopy characterizations of deposited films) were compared to theoretical calculations based in part on Pourbaix diagrams for these complicated systems. The authors conclude that a tungsten-induced codeposition mechanism adequately describes the formation of Co-W-P alloys.

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Functional Thin Film Molecular Sieving Materials

Separation of complex mixtures on the basis of the size of the component molecules has been used in synthesis and purification processes for many years. Further, molecular sieves such as zeolites are used as separators and catalysts in a number of industrial processes. As part of their studies of the use of discrete, nanoscale-cavity-containing, supramolecular coordination complexes as building blocks for functional thin film materials, researchers at Northwestern University in Illinois recently fabricated two new thin film molecular sieving materials composed of molecular squares with cavities as large as 2.5 nm. Junlian Zhang, Mary Williams, Melinda Keefe, Greg Morris, SonBinh Nguyen, and Joseph Hupp showed that these sieving materials are exceptionally porous to small molecules but block permeants larger than the square cavity size. Electrochemical experiments revealed that the size cutoff for molecular sieving could be altered by incorporating difunctional ligands within the square cavity responsible for the observed porosity. For one particular material (a salen-based zinc square utilizing pyridyl linkages), reducing the cavity dimension from 2.4 x 2.4 nm to 2.4 x 1.1 nm reduced permeabilities for appropriate probe molecules by factors of 1.5 to 4.

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Corrosion Control Using Polyelectrolyte Multilayers

Polyelectrolyte multilayers are a new class of organic thin films made by exposing a substrate to charged polymers in an alternating fashion. Held together by multiple electrostatic bonds, such films are rugged, easy to form, and are proving to offer a broad diversity of functionalities. Researchers at Florida State University recently reported that the corrosion of stainless steel under anodic conditions in salt solutions was strongly suppressed by an ultrathin film of polyelectrolyte multilayers. Voltammetric scans over a wide potential region, as well as constant potential measurements in the metastable pitting regime, reveal the effectiveness of the films at corrosion control. The anticorrosion property of polyelectrolyte multilayers is not only new but also surprising because the appreciable water content and ion permeability of these materials would typically be considered detrimental to anticorrosion

performance. This distinctive corrosion-resistance activity of polyelectrolyte thin films may be related to their ability to exclude small ions and decrease the chemical activity of water within the film. The authors envision several practical, large-scale applications of these films, including corrosion protection of the internal surfaces of piping systems, after construction, by a simple process involving alternate pumping of dilute aqueous solutions of polymers.

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Composite Proton Exchange Membranes for Fuel Cell Operation at Elevated Temperatures

Operation of proton exchange membrane (PEM) fuel cells at elevated temperatures is expected to confer a number of performance benefits, such as reducing the sensitivity of the fuel cell to poisons like carbon monoxide. Of course, these high operating temperatures presuppose the availability of a suitable PEM material. Toward this end, Adjemian, Lee, Srinivasan, Benziger, and Bocarsly at Princeton University in New Jersey have described their research aimed at extending the operational temperature range of PEM fuel cells. Their work focuses on new PEM materials that are composites of silicon oxide and Nafion. The silicon oxide was synthesized in the presence of the Nafion using a sol-gel method, and two approaches for introducing the silicon oxide into the Nafion were described: (1) synthesis of the oxide in a pre-existing Nafion membrane, and (2) formation and casting from a Nafion solution. In both cases, the authors report that the silicon oxide is uniformly dispersed in the nanoporous Nafion structure. This composite material exhibited improved water retention characteristics compared to the unmodified Nafion material and allowed for operation of a PEM fuel cell at temperatures as high as 130°C.

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Effect of Ammonia as a Potential Fuel Impurity on Proton Exchange Membrane Fuel Cell Performance

While the effects of traces of CO on the performance of PEM fuel cells have been extensively studied, little attention has been paid to other potential impurities from reformat gas. One possible contaminant, ammonia, is expected at concentrations between 30-90 ppm due to the high temperature reaction of H₂ and N₂ at available catalyst sites. Researchers at Los Alamos National Laboratory in New Mexico have reported that NH₃ can significantly degrade PEM fuel cell performance, with concentration and exposure time the primary factors controlling the behavior. A one hour exposure at concentrations as low as 13 ppm was enough to cause a 25% decrease in the current density while operating at 0.5 V, while 130 ppm resulted in a 60% drop. The use of pure H₂ fuel results in regeneration of performance after short exposure times; however, this method is not effective following longer NH₂ exposures. The authors conclude that the replacement of H⁺ with NH₄⁺, both in the catalyst layer and in the membrane, results in a conductivity decrease that contributes to the overall observed performance losses. They also suggest a possible solution via the use of an ion exchange resin to trap NH₃ from the contaminated fuel stream prior to use.

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Tech Highlights was prepared by Zenghe Liu of TheraSense, Inc., Venkat Srinivasan of The University of California, Berkeley, and Terry Guilinger, David Ingersoll, and Mike Kelly of Sandia National Laboratories.