

### Photoelectrochemical Study of Passive Film on Iron

Studies that seek to link aqueous corrosion behavior to a property of a protective metal oxide often rely on exposing a sample to electrolyte followed by an *ex situ* surface analytical measurement. An inherent shortcoming to this approach is the possibility of significant changes occurring in the oxide due to the dehydration process. The most straightforward approach to circumventing this problem is to use an *in situ* technique capable of providing information about near-surface properties. One such technique, photoelectrochemical spectroscopy, was recently used by Yu and coworkers at the University of Alberta and the University of Western Ontario to study the effects of hydrogen charging on the properties of iron oxide. In this study, photocurrent spectra were collected by measuring the magnitude of current as a function of the wavelength of incident light. The data were used to quantify the semiconductor properties of the oxide and to gain insight into oxide chemistry and structure. Degradation of corrosion performance with increased hydrogen charging was attributed, in part, to increased density of deep localized states, decreased bandgap, and increased disorder in the film. The presence of chloride in the environment did not significantly alter the photocurrent response for uncharged specimens, but caused a substantial decrease in the photocurrents measured on charged samples, suggesting a joint effect of hydrogen and chloride on the oxide properties.

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### Self-Annealing of Copper Interconnection Layers

Multilevel copper interconnection structures are used extensively in advanced integrated circuit architectures to realize a number of enhanced performance features. There is consequently great interest in developing improved methods for deposition of low-resistivity copper interconnect layers. Researchers at Hosei University in Japan have studied time-based variations in stress and resistivity of electrodeposited copper layers. High stress, high resistivity films deposited from copper sulfate plating solutions onto high stress TaN-a seed layers showed decreases in stress (from 33 to 28 MPa) and resistivity (from 2.9 to 2.4  $\mu\Omega\text{-cm}$ ) over a 1 month interval. These changes result from a self-annealing phenomenon that the authors attribute to an increase in grain size based on x-ray diffraction measurements. In contrast, low stress films (25 MPa) deposited from copper hexafluorosilicate solutions (even onto high stress TaN-a seed layers) do not self-anneal, as the stress remained unchanged with time.

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### Chemical Analysis of Graphite/Electrolyte Interface in Lithium Bis(oxalato)borate-Based Electrolytes

It is well known that the graphite anode commonly used in lithium-ion batteries can cointercalate solvent ions during operation, resulting in disintegration of the graphene planes (exfoliation). Ethylene carbonate is the only solvent known to protect against exfoliation in  $\text{LiPF}_6$ -based electrolytes, while graphite is particularly susceptible to exfoliation in  $\text{LiPF}_6$ -propylene carbonate (PC). As part of a continuing program aimed at exploring the utility of a new electrolyte salt, lithium bis(oxalato)borate (LiBOB), U.S. Army Research Laboratory researchers report that it can stabilize graphite anodes in PC-based electrolytes. In addition, LiBOB-based electrolytes were observed to have better stability at elevated temperature (70 °C). These observations suggest that LiBOB usage results in the formation of a stable solid electrolyte interface (SEI) layer that protects graphite. The authors used *ex situ* x-ray photoelectron spectroscopy to compare the SEI layer formed using  $\text{LiPF}_6$  and LiBOB in well-cycled graphite electrodes. They observed a signifi-

cant increase in SEI compounds containing carbonyl moieties when LiBOB was used. They conclude that the BOB anion participates in the formation of semicarbonate-like species in the SEI, and that these species are mainly responsible for the increased resistance to solvent cointercalation and disintegration.

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### Lewis Acid/Lewis Base Effects in Corrosion and Polymer Adhesion at Aluminum Surfaces

The surface properties of a metal are ultimately defined by the nature of its oxide film. In a recent paper by E. McCafferty of the U.S. Naval Research Laboratory, those properties are expressed in terms of the surface charge of the oxide, which is a function of its isoelectric point. At pH values below this point, the oxide is positively charged and it behaves as a Lewis acid, thereby favoring adsorption of Lewis bases (e.g., chloride). However, at pH values above the isoelectric point, the oxide is negatively charged and it behaves as a Lewis base; consequently, adsorption of Lewis acids is favored. The pitting behavior of aluminum in chloride solutions is presented to demonstrate this effect. As the pH becomes increasingly alkaline, the pitting potential is found to be roughly independent of pH until the isoelectric point is reached. At this point, the pitting potential increases to more positive values as the oxide becomes increasingly negatively charged (hence resisting chloride adsorption). Ion implanted aluminum surfaces in which the isoelectric point has been shifted exhibit the same behavior as a function of pH. Similarly, polymer adhesion is demonstrated to also be a strong function of the acidic or basic nature of the oxide films, with acidic polymers (e.g., PVC) adhering increasingly well to more basic surfaces and basic polymers (e.g., PMMA) to acidic surfaces.

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### Electrodeposition of Indium Antimonide

InSb is a III-V binary semiconductor being studied for high-speed applications in transistors and other devices because of its low effective electron mass and high mobilities. InSb is also used as an infrared (IR) filter and detector because its optical bandgap (0.17 eV) corresponds to an IR wavelength of 6.2  $\mu\text{m}$ . Researchers at National Cheng Kung University in Taiwan recently reported a study of the electrodeposition of InSb from an ambient-temperature molten salt. They performed the experiments in an ionic liquid of 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate with  $\text{InCl}_3$  and  $\text{SbCl}_3$  added at concentrations between 10 and 70 mM. InSb deposits formed by controlled potential electrolysis were characterized by x-ray diffraction and scanning electron microscopy. At a deposition temperature of 30 °C, InSb deposits were amorphous; however, polycrystalline InSb could be directly formed at 120 °C without additional annealing. The composition of the In-Sb codeposits was controlled by the concentrations of In(III) and Sb(III) in solution and by the deposition potential. At potentials where the deposition of In and Sb were mass-transport limited, InSb was formed when the ionic liquid contained equal concentrations of In(III) and Sb(III). IR absorbance spectroscopy measurements were used to determine the optical bandgap of this material, and the measured value of 0.20 eV is in close agreement with values reported in the literature.

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