

Atmospheric Corrosion of Carbonate Stone

Over the past several years, T. Graedel of Yale University has presented numerous reviews of the mechanisms of atmospheric corrosion of common engineering materials. In the March issue of the *Journal*, Graedel describes the atmospheric corrosion mechanisms of carbonate stones, such as limestone and marble. The primary distinguishing features of carbonate stone, compared to other materials, are its porosity (15-20% for marble) and the fact that calcium normally has only the +2 valence state available. The porosity allows not only freeze-thaw cycles to damage the material, but also water and any dissolved chemicals to have ready access to the interior of the material. In addition, the roughness and porosity provide convenient homes for a variety of biological organisms. The availability of only the +2 valence state considerably simplifies the mechanistic picture. The dominant corrosion products are sulfates and oxalates, the former resulting from interactions with atmospheric sulfur dioxide or sulfate ions, and the latter from the acid metabolites secreted by biological organisms such as algae and lichens. An interesting aspect of carbonate stone corrosion is that oxalates and sulfates tend not to occur together, most likely because the algae and lichens, which are the primary source of oxalates, are highly sensitive to the sulfur compounds that are commonly present in urban areas.

From: J. Electrochem. Soc., 147, 1006 (2000)

(Ed. Note: A book on Atmospheric Corrosion, authored by Graedel and Christofor Leygraf, will be published this coming August. The book is sponsored by ECS and will be published by John Wiley & Sons, New York.)

Simultaneous Detection of Temperature and Nitric Oxide Concentration Using a Single Sensor Element

The sensitivity of chemical vapor sensors to target gases is normally strongly dependent on temperature. For this reason, gas sensors usually need to incorporate an on-board temperature sensor to compensate for temperature fluctuations. Researchers in the Department of Applied Chemistry at Otta University in Japan began investigating capacitance-based sensors for nitric oxide (NO) that also had the capability to detect temperature changes. T. Ishihara, K. Kamakura, H. Nishiguchi, and Y. Takita found that a mixture of strontium-tin oxide and iron oxide ($\text{SrSnO}_3\text{-Fe}_2\text{O}_3$) could be used to simultaneously detect temperature and nitric oxide concentration. For this mixed oxide system, the capacitance of the device changed with NO concentration while the resistance of the device did not significantly change. Since resistance was not affected by NO concentration, the change in device resistance as a function of temperature could be used to monitor temperature fluctuations while the capacitance of the device was used to monitor variations in NO concentration. They also found that both the capacitance and resistance of the device were insensitive to such interferents as carbon monoxide, carbon dioxide, water, and methane.

From: Electrochem. and Solid-State Lett., 3, 245 (2000)

High Power, Common-Base GaN/AlGaN Heterojunction Bipolar Transistors

GaN/AlGaN heterojunction bipolar transistors (HBTs) are being investigated for possible use in satellite, radar, and communication applications. Some of these applications require the ability to operate at frequencies of 1-5 GHz, at temperatures above 400°C, and at powers greater than 100 watts. A research team from the University of Florida and SVT Associates in Minnesota has reported the first common-base operation of a GaN/AlGaN HBT. The multilayer structure was grown by molecular beam epitaxy using Ga, Al, and plasma-activated nitrogen. The substrate was 2 μm GaN grown by metallorganic chemical vapor deposition (MOCVD) on a sapphire substrate. While current gain for HBTs

are greater than unity only in the common-emitter mode, the authors point out that the common-base mode has the possibility of appreciable power gain obtained through the impedance transformation offered by the amplifier. This is the first report of power densities in GaN/AlGaN HBTs, and the devices had excellent high temperature characteristics. At 250°C, the transistors had a maximum current density of 2.55 kA/cm² at VBC = 4 volts, for a power density of 10.2 kW/cm². Further enhancements in device performance are expected with improved methods for GaN and AlGaN surface passivation.

From: Electrochem. and Solid-State Lett., 3, 144 (2000)

Methanol Sensor for Use in Fuel Cell Power Sources

Direct methanol fuel cells (DMFCs) have been the subject of considerable research during the last decade. Advances in power density, efficiency, and lifetime have made this technology a promising power source for a variety of portable applications. At the Jet Propulsion Laboratory (JPL) in California, a 150 W packaged power source based on DMFCs is currently in development. Practical operation of this power source, as well as others based on the direct oxidation of methanol, requires accurate sensing, monitoring, and control of methanol concentration. Narayanan, Valdez, and Chun at JPL have reported a robust, sensitive, and quick-responding sensor technology for accurate measurements of methanol concentration in an operating DMFC system. The amperometric sensor is based on the oxidation of methanol (to carbon dioxide) at a Pt/Ru anode on a Nafion 117 membrane. A Pt black cathode, which supports hydrogen reduction and serves as a pseudo-reference electrode, resides on the other side of the membrane. The sensor responds in less than 1 second and detects concentration changes as small as 0.01 molar. In addition, the robustness of the sensor was demonstrated in a 70-hour test where the sensor was integrated, as an element of an automatic feedback system for methanol concentration measurement and control, into an operating DMFC system.

From: Electrochem. and Solid-State Lett., 3, 117 (2000)

Photocorrosion of Copper in the Damascene Process

The copper damascene process is expected to find widespread use in the fabrication of multi-level interconnects in new chip architectures, and a key to its successful implementation is chemical mechanical polishing (CMP) of copper and barrier materials. Researchers at Hitachi, Limited in Japan have reported a detailed study of copper corrosion in alumina-based CMP slurries containing hydrogen peroxide. They noted evidence of both chemical and galvanic corrosion mechanisms. These mechanisms are well-understood, and methods for mitigating them (*e.g.*, addition of a benzotriazole inhibitor) are known. In addition, pattern-specific corrosion was found when the damascene process was used to make copper interconnections in integrated circuits. Copper deposited on p+ diffused regions is positively biased with respect to copper on the n+ region of the p-n junction. The authors found that the positively-biased copper was quickly corroded in the CMP slurries, and that photoillumination was a major contributor to the observed bias. Addition of inhibitors to the slurry did not reduce the corrosion rate, and the authors concluded that less corrosive slurries or improved cleaning methods to rapidly and efficiently remove the slurry from the device region, will be required.

From: J. Electrochem. Soc., 147, 1193 (2000)

Tech Highlights was prepared by Vicki Edwards of Corning, Inc., and Terry Guilinger and Mike Kelly of Sandia National Labs.