TECH HIGHLIGHTS

Improved Understanding of Parameters Contributing to Corrosion Resistance of Sputtered Al Thin Films

Evaporated and sputter-deposited thin metal films are technologically important as interconnect materials in the semiconductor industry. For reliable performance of microelectronic devices, it is essential to understand the processing/structure/property relationships that contribute to good corrosion resistance. Gerald Frankel and his collaborators at The Ohio State University, and at Monash University and the Melbourne Centre for Nanofabrication in Australia, recently reported their study of the effect of vacuum system base pressure on the corrosion resistance of sputtered aluminum thin films. They deposited 100- nm films at four different base pressures, and characterized the film properties by potentiodynamic polarization, sheet resistance measurements, thin film pit growth experiments, x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Interestingly, the best corrosion resistance was observed with thin films deposited at the highest base pressure (*i.e.*, the worst vacuum), as shown by shifts in the pitting and repassivation potentials in the noble direction with increasing base pressure. In addition, XPS showed an increase in the Al^{3+}/Al^0 ratio and TEM showed an increased oxygen content when the base pressure was increased, perhaps as a result of oxidation of the thin film in the deposition chamber. Among the authors' conclusions is a recommendation to perform depositions at a maximum base pressure in the low 10^{-7} Torr range for optimal thin film properties.

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Chemical Vapor Deposition of Copper: Use of a Molecular Inhibitor to Afford Uniform Nanoislands or Smooth Films

Thin films of copper can be deposited by various techniques such as wet chemical growth, vapor deposition or atomic layer deposition. The smoothness of the film depends upon the substrate. Cu(hfac)VTMS (hfac = hexafluoroacetylacetonate, VTMS = vinyltrimethylsilane) is a common precursor used in the chemical vapor deposition (CVD) of the copper. Sometimes, water addition or plasma enhanced CVD is used to improve the smoothness of the copper films. In the present investigation, Shaista Babar et al. propose a new technique to obtain not only the smooth surface but also to vary the morphology of the film as per demand. The results demonstrate that the VTMS serves as a growth inhibitor for copper CVD from Cu(hfac)VTMS. If the VTMS inhibitor is used during the nucleation stage, the deposited copper film exhibits the features of Cu islands with a relatively uniform size distribution. A continuous, smooth (rms roughness <1.5 nm) thin film can be obtained if the nucleation is done in the absence of inhibitor. These results could be of interest for the production of textured films for photonic applications in the microelectronics industry.

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$Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$: "Bi-Functional" Electrode Materials for Na-Ion Batteries

While lithium ion battery chemistries have attained, widespread commercialization and continue to enjoy continued research and development efforts, some researchers, foreseeing a time of limited lithium resources, are prompted to explore other battery chemistries similar to lithium ion, but based on abundant and environmentally friendly elements. One set of researchers from Michigan State University has chosen to investigate $Na_{2/3}(Ni^{2+})_{1/3}(Ti^{4+})_{2/3}O_2$ (SNTL). SNTL is a "bi-functional" electrode material in that the material can serve as either cathode by having the high-voltage Ni^{2+}/Ni^{3+} redox couple activated, or anode by having the low-voltage Ti^{4+}/Ti^{3+} redox couple activated. The authors found these redox potentials were ~3.7 V and ~0.7 V (vs. Na/Na^+), respectively. X-ray diffraction confirmed that no other phases evolved during cycling in the $x = 1/3$ to 1 range (where x represents the atomic fraction of Na in the oxide material), thereby demonstrating that the reaction is by intercalation; however, another phase formed when the SNTL half cell was charged to 4.5 V, where more sodium ion was extracted such that $x < 1/3$. Rate capability tests demonstrated that 75 mAh/g was achievable at a C/20 rate for both electrodes. Cycling studies revealed capacity fade, especially for the anode. With further work, the authors see promise for SNTL serving as both cathode and anode in a 3-V Na-ion cell.

From: *ECS Electrochem. Lett.*, 3, A23 (2014).

Effect of Mechanical Compression on Chemical Degradation of Nafion Membranes

A chemical reaction may be activated by mechanical stress (pressure) as well as by thermal and electrical energies. Researchers at the Lawrence Berkeley National Laboratory (LBNL) have expanded their studies of the effect of pressure on membrane films by investigating the effect of compression on the chemical degradation of Nafion membranes. While accelerated stress tests typically enhance a single failure mode, combined chemical and mechanical stressors, as experienced in fuel cell operation, may have synergistic interactions and not simply result in additive effects. Fenton's test, comprising hydrogen peroxide and an iron catalyst, was used to release fluoride ions from the membrane's fluorocarbon chains while the Nafion membrane was compressed between platens of a mechanical press set to various pressures. The measured fluoride release rate revealed an increased degradation rate with pressure in the low to 10 MPa range. These same membranes were subsequently re-protonated and soaked in water before being placed in a beamline at the Advanced Light Source (ALS) for small-angle x-ray scattering (SAXS) experiments. The domain spacing between hydrophilic ion-rich water domains was found to increase with increased degradation, leading the authors to postulate that synergistic chemical/mechanical stressors effected changes in the morphology as well as chemical structure.

From: *ECS Electrochem. Lett.*, 3, F33 (2014).

Carbonized Wood for Supercapacitor Electrodes

Electrochemical supercapacitors offer high power density charge storage, but compared to Li-ion batteries, they have limited energy densities. In supercapacitor research and development, advancements are largely focused on energy density improvement, but the financial and environmental costs could also be reduced through innovative use of active materials. Researchers at the University of Utah have demonstrated the remarkable possibility of utilizing carbonized wood materials as inexpensive, high performance supercapacitor electrodes. The high surface area required for useful power densities is provided by the three-dimensional network structure formed by interconnected micro-channels after carbonization of three different varieties of wood. Charge-discharge cycling tests in a KOH electrolyte solution demonstrate that carbonized woods offer a maximum energy density of ~45.6 Wh/kg (discharge current of 200 mA/g). These electrodes also exhibit a maximum power density of ~2000 W/kg at a discharge current of 4000 mA/g, but with limited energy densities. The carbonized wood supercapacitor electrodes also exhibited very good cyclability, and retained 99.7% of the specific capacitance after 2000 cycles. The work demonstrates the principle of exploiting the high surface area of a series of carbonized woods, for environmentally friendlier supercapacitor electrode materials that do not require extra binders to function as active electrodes.

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