# **TECH HIGHLIGHTS** •

## Green Fluorination of Natural Graphite and Its Applications in Rechargeable Magnesium Ion Transfer Batteries

Natural graphite has been electrofluorinated using triethylamine tri(hydrofluoride)  $(C_{2}H_{2})$ , N·3HF, and the fluorinated graphite has been demonstrated as a cathode in a rechargeable Mg cell with specific capacity of 548 mAh/g. The electrochemical method of fluorination avoids safety issues in handling fluorine from other sources, such as  $F_{2}$ ,  $CF_{4}$ , CHF<sub>3</sub>, and C<sub>3</sub>F<sub>8</sub>. Researchers from India employed cyclic voltammetry to fluorinate graphite electrochemically and showed by SEM that the fluorinated carbon has smaller flakes than nonfluorinated carbon. The authors demonstrated discharge capacity and cycling by discharging a cell comprising a fluorinated graphite sheet as the cathode, a magnesium electrode as anode, and an electrolyte of 1 M magnesium perchlorate in dimethyl sulfoxide (DMSO) from 2.7 V to 1.0 V. They obtained discharge capacities of 548 and 348 mAh/g at 0.5 and 0.75 mA/g, respectively. A gradual decrease in the discharge capacity was reported and caused by irreversible reduction of CF at potentials higher than 2 V. Fluorinated carbon is believed not only to enhance reaction rates, but also to allow preservation of more magnesium than that in the virgin graphite. Magnesium ion intercalation and deintercalation could occur through the edge planes of graphite or pass through the cracks on the basal plane formed by electrochemical fluorination.

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## Atomic Layer Deposition of High-k Dielectrics on Sulphur-Passivated Germanium

High mobility channels are being actively investigated for future complementary metaloxide semiconductor (CMOS) technology nodes, as a potential replacement for standard silicon channels. A significant issue is that carrier mobilities can be adversely affected by a poor passivation of the interface between the gate dielectric and the conducting channel. This can also limit the transconductance in CMOS devices. Researchers from IMEC in Belgium, and collaborators, successfully terminated oxide-free Ge by S-passivation using an (NH<sub>4</sub>)<sub>2</sub>S treatment. The resulting Ge-S surface was mostly retained during successive high-k dielectric stack atomic layer deposition (ALD), with a caveat that the first dielectric layer should be closed prior to subsequent ALD stack growth. In addition, the team found that the Ge/S/Al<sub>2</sub>O<sub>2</sub> interface is superior to both Ge/S/ ZrO, and Ge/S/HfO, interfaces. In Ge/S/Al<sub>2</sub>O<sub>2</sub>/ HfO, or Ge/S/Al<sub>2</sub>O<sub>2</sub>/ZrO<sub>2</sub> bi-layer stacks built by the team, the Al<sub>2</sub>O<sub>2</sub> thickness was reduced to a minimum without degradation of the interface properties, even with thick deposits since Al<sub>2</sub>O<sub>2</sub> ALD seeds as islands on the S-terminated Ge surface. The technological approach was vetted, however, when the researchers built a p-type metal-oxide semiconductor fieldeffect transistor (pMOSFET), using a bi-layer

gate stack comprising Ge/S/Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub>. The device showed a promising peak mobility of  $>200 \text{ cm}^2/\text{V}\cdot\text{s}$  at an equivalent oxide thickness (EOT) of 1.5 nm.

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#### Development and Application of Transport Modeling in Direct Methanol Fuel Cell Diffusion Layers

Direct methanol fuel cells (DMFCs) are an appealing power source for portable devices as they exhibit high energy density, have low refuel times, and operate at relatively low temperature; however, their design properties must be optimized if they are to achieve their efficiency potential. Researchers in Texas have developed a one-dimensional, two-phase model of methanol, water, and carbon dioxide transport in the DMFC anode diffusion layer for the purpose of analyzing DMFC performance sensitivity to variations in the layer's physical properties. Their model predicts that thick diffusion layers with small absolute permeability promote a low methanol concentration at the catalyst layer and a high pressure gradient across the anode diffusion layer. Minimizing the methanol concentration at the anode catalyst layer increases efficiency by decreasing undesirable methanol crossover to the cathode catalyst layer, and increasing the gas phase pressure gradient across the anode diffusion layer promotes the removal of carbon dioxide produced at the anode from the DMFC system. The model anticipates a significant portion of the methanol and water flux to be in the vapor phase at higher current densities and temperatures. Therefore, they recommend that the physical properties of commercial DMFC anodes should be optimized for these two operational parameters.

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# Electrophoretic Fabrication and Characterizations of Manganese Oxide/Carbon Nanotube Nanocomposite Pseudocapacitors

Innovations in charge storage devices have brought enhancements in energy capacity, device lifetime, and cost efficiency, among other important benchmarks. An important characteristic of these devices that demands continuous advancement is the suppression of electrical degradation due to charge/discharge cycling. One path toward improved cycle performance involves improved materials continuity at the microscale and nanoscale. To achieve this, many in the electrical storage community have explored the production of nanostructured materials that exhibit high chemical integrity while possessing desirable electronic properties. Researchers from the National Chiao Tung University in Taiwan tackled this topic by exploring the fabrication of nanostructured composites of mixed-phase manganese oxide (MnO<sub>x</sub>) and multiwalled carbon nanotubes (MWCNTs) to be employed as electrodes for pseudocapacitors. To facilitate the desired integration of the composite into

metallic substrates, the scientists employed electrophoretic deposition to embed the MnO<sub>2</sub>-MWCNTs composites directly into nickel-based electrodes. This process achieved enhancements in the redox reaction area of the electrodes and major improvements in the pseudocapacitance as a function of charge/ discharge cycling (> 80% maintenance over 6000 cycles) compared with previous experiments. These enhancements evolved as a function of composite annealing temperature, reaching a maximum at ~200 °C; this provides substantial encouragement for the development of low cost pseudocapacitors, comprised of MnO -MWCNTs composites that exhibit high cycling stability and increased specific capacitance for electronic device applications.

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# Die-to-Die Adhesive Bonding to Produce Evanescently-Coupled Photonic Devices

The integration of photonic devices with silicon-based microelectronic circuits holds promise for the production of a new generation of powerful device technologies. Since the fabrication of efficient light sources in silicon is hampered by silicon's indirect band gap, it is highly desirable to integrate silicon with III-V semiconductor optical devices. Researchers at Intel Corporation in Santa Clara, California and at Ghent University-IMEC in Belgium have reported a new process for bonding III-V dies and silicon-on-insulator (SOI) photonic waveguides. Instead of direct bonding of the III-V die and the pre-patterned SOI waveguide (e.g., by plasma assisted wafer bonding), the authors demonstrated that a thermosetting polymer, divinylsiloxane-bisbenzocyclobutene (DVS-BCB), can be used to produce a strong, uniform, and thin (< 100 nm) adhesive bond suitable for the production of evanescently-coupled photonic devices such as hybrid III-V/Si lasers. They focused their research on a process that could be scaled up to a multiple die-to-wafer bonding procedure where III-V dies would be bonded to a full SOI wafer. Based on characterization of the bonding process and the properties of the bonded assemblies (as determined by electron microscopy, optical profilometry, and lap shear testing), the authors believe their new process could potentially be matured into a full-scale industrial process.

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Tech Highlights was prepared by Mike Kelly of Sandia National Laboratories, Colm O'Dwyer of University of Limerick, Craig Walker of Valence Technology, Inc., James Dickerson of Vanderbilt University, Arnold Stux, and Donald Pile of Dow Kokam LLC. Each article highlighted here is available free online. Go to the online version of Tech Highlights, in each issue of Interface, and click on the article summary to take you to the full-text version of the article.