High-Dielectric-Constant Oxide $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ Forms as a Disordered Perovskite

P. Jha and A. Ganguli of the Department of Chemistry at the Indian Institute of Technology, S. Bobev at Los Alamos National Laboratory, and G. Subbanna in the Materials Research Center at the Indian Institute of Science have prepared and characterized an oxide with the formula $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ in an attempt to produce an oxide with a high dielectric constant and low dielectric loss.

As reported in the June 3 issue of *Chemistry of Materials*, the oxide was prepared by a high-temperature ceramic route at 1200°C and characterized by x-ray, neutron, and electron diffraction studies as well as by scanning electron microscopy and studies of the frequency and temperature—dependence of the dielectric properties. The diffraction studies indicate that the oxide has a disordered perovskite structure with a cubic cell lattice parameter of ~3.94 Å, significantly less than the ~4.00 Å lattice parameter of the simple cubic perovskite $BaTiO_3$.

The preliminary characterization of the dielectric properties of $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ is promising, according to the researchers, as the compound displays a combination of high dielectric constant, low dielectric loss, and stability with regard to frequency. At 100 kHz, the dielectric constant varied from 59 (at 35°C) to 62 (at 300°C). The corresponding dielectric loss at these temperatures varied from 0.0047 to 0.03033. The researchers said that there is likely a loss peak at or near 500 kHz. Furthermore, the dielectric constant was nearly stable over a frequency range of 0.5–500 kHz at room temperature. Additional characterization studies are needed to determine the thermal expansion, mechanical strength, and optimal thin-film fabrication conditions.

From a materials standpoint, oxides with complex perovskite structures hold tremendous interest. Their promise as advanced materials for applications as magnetic materials, superconductors, and dielectrics has motivated their development. A variety of rare-earth copper titanates have been synthesized earlier in the search for high-temperature superconductors wherein the partially filled copper *d*-band holds potential for creating novel conducting or superconducting materials.

In the present study, the researchers were more interested in dielectric properties of the oxides. As a consequence, they introduced closed-shell zinc in place of the open-shell copper with the goal of producing a high-dielectric-constant material with low dielectric loss.

"We are excited by the potential for this new oxide as a very efficient dielectric, especially in the microwave region," said Ganguli. "We look forward to exploring the range of properties of this material and hope to find it suitable for the electronic industry. New materials continue to pave the way for exciting new technologies, and I am hopeful that $Nd_2Ba_2CaZn_2Ti_3O_{14.4}$ will be useful in this respect."

EMILY JARVIS

Control of Injected Spin Reduces Semiconductor Laser Threshold

Current research in the area of semiconductors reveals that spintronics—electronics that exploits the spin of an electron in some way, rather than just its charge—will open new avenues in device development. As reported in the June 16 issue of *Applied Physics Letters*, a group of researchers led by J. Rudolph at Universität Hannover, Germany, and H.M. Gibbs from the University of Arizona have demonstrated a 23% reduction in the laser threshold, as compared with conventional unpolarized electron pumping, by optically pumping spin-polarized electrons in the gain medium. Using theoretical modeling of the structure, the researchers were then able to generalize the concept to an electrically driven device for which room-temperature optimized guidelines were proposed. They said that a reduction in laser threshold of up to 50% may be achievable in electrically pumped devices.

The laser structure relies on the use of quarter-wavelength distributed Bragg reflectors at the top and bottom, which serve as laser mirrors. A pair of InGaAs quantum wells (QWs) was fabricated in the optical nodes of the laser cavity to increase the efficiency of the optical gain momentum. The electrons and holes were optically excited in the QWs by laser pumping in the growth direction with circularly polarized femtosecond pulses of a mode-locked Ti:sapphire laser at a frequency of 80 MHz and a wavelength of 780 nm. The excitation energy was selected such that transitions from the heavy and light hole bands to the conduction band were possible, but not transitions from the spin-split band to the conduction band, which resulted in an initial spin alignment of about 50%. Measurements were performed at 6 K using a He vapor cryostat. A higher intensity of emitted light was recorded, as compared with the classical unpolarized case, which the researchers attributed to the predominant spin-polarized contribution that is characteristic of the circularly polarized excitation. No spin-effect contribution from the holes was considered, due to the rapid spin dephasing from the fast heavy/light hole mixing. The laser threshold for the spin-aligned emission was 0.5 A/cm^2, which is substantially lower than the 0.65 A/cm^2 measured for randomly oriented spins.

To verify the strong dependence of the spin orientation, the researchers measured the change of emitted intensity for fixed pump power and continuously changed the degree of spin orientation by changing the polarization of the excitation laser. The modulation of the degree of spin orientation from −50% to +50% resulted in an intensity modulation of 400% in the emitted laser radiation, showing the strong correlation between spin alignment and the process dynamics.

Using theoretical calculations based on a three-level model—pump level, lasing level, and ground state—the researchers concluded that a spin vertical-cavity surface-emitting laser will also operate with very fast pulsed or continuous electrical pumping, displaying improved threshold reduction, as compared with optical pumping. Additionally, the dephasing time was found to be long in spintronics laser devices, as compared with the reduced carrier lifetime in the simulated emission regime. The researchers expect that the electrically pumped, room-temperature spin laser will advance to commercialization once room-temperature spin injection with improved spin alignment is achieved.

CALIN MICLAUS

Self-Assembled Monolayer of Organic Molecules Adsorbed on Gold Substrate Induces Magnetism

Researchers at the Weizmann Institute in Israel have demonstrated magnetism at room temperature in organized close-packed thio-organic films adsorbed on gold substrates. This finding is of interest for the development of electronic devices where the ability to modify electronic properties of substrates is necessary. R. Naaman and co-workers reported in the June 15 issue of the *Journal of Chemical Physics* that the magnetism appears to arise from the self-assembled monolayers of organic molecules on the metal substrate. Most significant, said the researchers, is that many spins are polarized per adsorbed molecule.

The researchers investigated three types of films bound to the gold: a two-carbon-chain ethylthiol, an 18-carbon-chain alkylthiol, and polyalanine containing 22 amino acid residues. Characterization methods—including infrared spectroscopy, ellipsometry, atomic force microscopy, and x-ray photoelectron spectroscopy—revealed that in the latter two cases, an organized close-packed monolayer formed on the substrate. The ethylthiol layer, while not well organized, also formed a full monolayer.

Magnetism measurement using a superconducting quantum interference device (SQUID) not only demonstrated magnetic properties, but also revealed magnetic moments in the polyalanine sample that exceeded several tens of Bohr magnetons per adsorbed molecule. When the researchers studied organothiols adsorbed on a GaAs(100) surface, a close-packed monolayer was formed, but it did not produce a magnetic response.

"The results presented here demonstrate a new type of magnetic property *ex nihilo*, for organic monolayers self-assembled on gold, namely, magnetism is obtained for systems where none of their components is magnetic," said the researchers.

The researchers account for the magnetic moments by means of a charge transfer between the organic layer and metal substrate of unpaired electrons on the organic molecules. "Since each organic molecule has, at most, two unpaired electrons (triplet state)," they said, "the observed spins are the outcome of polarization of conducting electrons within the metal."

Electrical Current Imaging Technique Reveals Line Flaws at Submicron Level

University of Maryland researchers at the College Park and Baltimore County campuses have developed a technique for imaging electron flow, based on the magnetic force microscope, that has the potential to pinpoint heretofore invisible flaws in nanoscale integrated circuits (IC). In the May 12 issue of *Applied Physics Letters*, they describe how the imaging technique reveals a phenomenon called current crowding, where current flow along a conducting pathway becomes "bunched up" when it hits a flaw in the line. Current crowding can exacerbate such flaws and, in concert with other environmental factors, lead to line breaks that in turn cause IC failure.

To obtain a complete and fundamental understanding of electromigration failure in submicron metallic lines, investigators have experimentally studied the nature of current crowding in the vicinity of model defect structures that simulate voids or other current-deflecting entities. Until recently, there has been no quantitative method that permits direct imaging of current distributions in metallic structures at the micron scale and below. The imaging method developed by E.D. Williams, director of the university's Materials Research Science and Engineering Center (MRSEC), and co-workers relies on inversion of results from standard magnetic force microscopy (MFM) measurements, making it possible to deduce underlying current densities.

To validate their MFM-based technique, the researchers fabricated interconnect samples consisting of a pair of chromium/gold lines on a silicon dioxide substrate. They then used focused ion-beam milling to cut an angled slit in the side of one line and a triangular notch in the side of the other, creating sample defects that simulate structures observed in prior studies of electromigration failure. MFM images showed high contrast at the inside edges of the fabricated defects, indicating highly localized current density, or current crowding. While both defects block the same fraction of line width and have the same 45° orientation on one of their sides, the slit, with its undercut orientation, shows much stronger magnetic-field curvature than the notch, indicating greater current crowding. Therefore, according to the researchers, the technique provides insight into how varying flaw shapes affect current crowding even when the same degree of current constriction takes place.

While MFM offers submicron spatial resolution unmatched by other methods,

it is difficult to quantify the signal measured, said the researchers. They measured magnetic-field curvature instead of the direct field, which is convoluted or blurred by the effects of the instrument. They then performed an inversion procedure, which they adapted for micron-scale data, to yield the sheet current distribution within the sample. This approach is analogous to that developed for magnetoresistive and magneto-optical imaging of critical current densities in millimeter-scale superconducting strips and tapes.

As expected, in regions far from the defects, MFM shows current uniformly distributed across the line with no current flow perpendicular to the line edges. But where current must curve around a defect, there is a component of perpendicular flow localized within 5 μm of the defect. The current crowding in the vicinity of the defects is resolved as a marked concentration of current at the apex of each defect, the researchers said. The crowding region extends ~1 μm from the inner edge of the angled slit defect and ~2 μm from the triangular notch. The peak current density in the crowding region of the slit is 3.9 times larger than the average current density far from the defect, while it is 3.1 times larger than the average for the notch. The imaged current distributions are in agreement with calculations made of models of the lines, confirming the fidelity of the MFM imaging method.

While the dimensions of the sample lines and defects used in this investigation were at the micron scale, the MFM technique's submicron lateral resolution may be extended to make it suitable for use with 100-nm-scale features, said the researchers.

The researchers said their technique holds potential as a diagnostic tool with 50 nm current resolution for IC design, development, and manufacturing, and as a forensic tool to analyze failures in chips already manufactured and deployed.

Quantum Chemical Molecular-Dynamics Simulation Demonstrates Fullerene Formation

Although fullerenes are now commonplace, their mechanism of formation remains in the realm of speculation. The numerous mechanisms put forth in the literature hypothesize that fullerenes are either constructed stepwise from carbon fragments or are spontaneously formed by a collapse of a highly organized structure. An important structural requirement is thought to be the introduction of pentagons into the hexagonal graphite lattice to develop curvature. A few attempts have been made to simulate fullerene formation by means of classical molecular dynamics (MD), that is, using empirically derived force fields. However, these studies lack the consideration of quantum chemical delocalized potentials necessary to describe π-conjugational effects—the critical ingredient in carbon nanochemistry that is dominated by sp^2-hybridized carbon atoms. Recently, however, a team of researchers from Emory University, Georgia, and from Universität Paderborn and Abteilung Molekulare Biophysik in Germany has simulated the formation of fullerenes from single-walled carbon nanotubes using quantum chemical potentials. These researchers assert that other recent quantum chemical attempts at locating transition states of chemical pathways are implicitly incorrect because they represent hypothesized pathways and do not take into account the specifics of chemical systems far from thermodynamic equilibrium.

In an article published in the April issue of *Nano Letters*, Emory University researchers S. Irle, G. Zheng, and K. Morokuma, and M. Elstner from Germany, employed quantum chemical MD simulations to identify key steps in fullerene formation. Morokuma and co-workers used three different types of (n,m) open-ended carbon nanotubes with similar diameter d as initial structures: armchair (5,5), d = 6.88 Å; chiral (7,3), d = 7.15 Å; and zigzag (9,0), d = 7.06 Å. Tube lengths of 7.5 Å, 10 Å, and 20 Å were chosen for each species. A (10,5) nanotube with d = 10.5 Å was also simulated, but it proved to be too large to form fullerenes, regardless of tube diameter, during the 12 ps allowed for this simulation. The all-valence electronic structure calculations were performed with a density functional tight-binding (DFTB) method, which is computationally inexpensive enough to obtain trajectories of 20 ps or longer. DFTB approximates density functional theory and involves no fitting to experimental data.

The end of a tube was deemed closed when not more than eight carbon atoms constituted the largest rings present in the opening. When both ends are closed in this manner, a fullerene molecule is formed. The researchers observed that temperature is the most important factor for the formation of fullerenes. Simulations performed at 1000 K proved nonreactive on the time scale of tens of picoseconds, and those performed above 4000 K frequently led to nanotube fragmentation. Although Morokuma and co-workers acknowledge that the use of carbon nanotubes as initial structures is somewhat artificial, they find it striking that many nanotubes simulated at 3000 K and 4000 K closed at both ends and formed fullerenes within 14 ps. An important dynamic event common to many of the simulations is the formation of "wobbling" acetylenic C_2 units (i.e., C_2 fragments unattached on one end) that occasionally catch neighboring hexagons to form pentagons and thereby restructure the tube opening. The researchers said that the time required for tube closure does not appear to depend on the tube length.

Morokuma and co-workers believe that their findings are generally applicable to any carbon cluster with a high degree of curvature. They are confident that they can apply this computational approach to a more realistic model system, initially comprised entirely of C_2 molecular units, and follow cluster formation and cage closing "from scratch."

STEVEN TROHALAKI

Blue-Emitting Polymers Synthesized

Electroluminescent polymers are promising materials for light-emitting diode (LED) and display applications. Currently, the most potentially useful polymer for these applications, poly(*p*-phenylenecyanovinylene) (CN-PPV), derives its electron-transport properties from the electron-withdrawing cyano groups attached to the polymer backbone. Y. Liu, D. Zhu, and co-workers at the Institute of Chemistry in the Chinese Academy of Sciences have prepared novel electron-transporting copolymers of cyanostilbene (CN) with fluorene (F), binaphthyl (BN), and benzyl (Ph) units. An LED device fabricated using the F-CN copolymer exhibited good diode behavior and emitted blue light with external quantum efficiencies of 0.006% and 0.2% for single- and double-layer structures, respectively. According to Liu, "Once these efficiencies are improved by optimizing the device structure, the copolymers may find application as electron-transporting or hole-blocking materials in LEDs."

As reported in the May 20 issue of *Chemistry of Materials*, the copolymerization of the monomers with cyanostilbene to produce Ph-CN, F-CN, and BN-CN was carried out by the palladium-catalyzed Suzuki coupling reaction. The reactions exhibited yields of 79–90%, and produced polymers with average molecular weights of 32820–38110. These values are 8–10 times higher than those reported for CN-PPV. The polymers' lowest unoccupied molecular orbital and highest occupied molecular orbital levels were measured to be from –2.92 eV to –3.08 eV, and from –6.01 eV to –6.13 eV, respectively. These energy levels are low enough for the polymers to be used as hole-blocking materials in LED devices. All of these polymers possess excellent thermal stability, with glass-transition temperatures of 60–159°C and onset decomposition temperatures of 411–417°C.

The researchers also found that the optical properties of the copolymers can be systematically modified. Absorption and photoluminescence (PL) measurements in solution and thin films indicate that changing the backbone alters the conjugation length of the polymer and allows the tuning of its absorption and emission peak wavelength in the 457–489 nm range. The PL spectra of the copolymers also have much narrower peaks than those of CN-PPV, due to the absence of aromatic ring stacking in the polymer backbone.

Greg Khitrov

Nanotube FET Detects Streptavidin

Field-effect transistors fabricated using semiconducting single-walled carbon nanotubes (SWCNTs) are attractive devices for use as gas and chemical sensors. Electronic sensors based on carbon nanotubes are also promising for biological detection because of the tubes' small size, fast response, and selectivity ability as well as the easy charge transfer between analytes and nanotube. In the April issue of *Nano Letters*, A. Star and co-workers from Nanomix Inc. have reported the creation of a sensor for streptavidin. The researchers functionalized a nanotube field-effect transistor (NTFET) sensor with a coating of poly(ethylene imine)/poly(ethylene glycol) (PEI/PEG). Biological specificity is gained by modifying the PEI polymer with biotin molecules. Nonspecific binding of the biomolecules (streptavidin) is prevented by the PEG component of the polymer coating. The initial coating of polymer shifts the device characteristics of the NTFET from *p*- to *n*-type, and biotinylation of the polymer recognition layer returns the device to *p*-type. After incubation with streptavidin, the nanotube sensor shows a decrease in conductivity. This change in electrical behavior is the sensing mechanism for detecting specific protein binding.

The nanotubes were grown from a $CH_4 + H_2$ mixture using an Fe catalyst on a 100 mm silicon wafer coated with 200 nm SiO_2 at 900°C. This procedure results in the formation of SWCNTs that are 5–10 μm long and 1.5–3 nm wide. All contacts and connectors for the NTFET were made by the optical lithography technique. The source and drain of the NTFETs were connected by multiple nanotubes. Several types of devices based on different semiconducting media (CNTs, CNTs coated with PEI/PEG, and CNTs coated with PEI/PEG with biotin labels) were prepared as sensor and control experiments. Only devices based on the CNTs coated with PEI/PEG with biotin labels show significant sensitivity to streptavidin. The current at –10 V gate voltage changed by a factor of 4 (from ~0.2 to ~0.8 μA) for devices with and without streptavidin. This response is encouraging for the further development of NTFETs for biological detection. For instance, the researchers estimate that with proper modification of the polymer recognition layer, the detection of a single biological molecule should be possible.

Maxim Nikiforov

Nanodiamond Cyclohexamantane ($C_{26}H_{30}$) Isolated from Petroleum

J.E.P. Dahl of ChevronTexaco Energy Research and Technology, with an international group of researchers, has characterized and verified the structure of cyclohexamantane, of the class of molecules known as diamondoids. Diamondoids are unusual hydrocarbons with a cagelike carbon atom arrangement that corresponds to sections of the crystal structure of diamond. As reported in a communication in *Angewandte Chemie International Edition* **42** (2003), the cyclohexamantane framework consists of 26 carbon atoms, with 30 hydrogen atoms occupying the corners of the carbon cage.

Nanodiamonds possess the strength and stability of diamonds, but the different structures of their molecules provide structural diversity that makes them ideal building blocks for nanotechnology, said the researchers. In principle, the corner atoms could also be equipped with different functional groups, which would result in chemical versatility.

The research team from ChevronTexaco, BP, Pfizer, Stanford, Cornell, the University of California—Davis, the University of Bristol, and the U.S. Geological Survey isolated $C_{26}H_{30}$ from petroleum but has not been able to produce cyclohexamantane synthetically.

Dahl said, "How cyclohexamantane is formed remains unclear; however, the reaction pathway which leads to [its] formation could also have led to larger diamondoids, even to microcrystalline diamonds. We are currently testing this hypothesis." ☐