grew on each Ni tip, the field-emission measurements were specific to individual nanotubes for two reasons. First, the emission current (I_{FE}) is an exponential function of field, so only a few MWNTs are able to emit. Second, the geometry of field emission allows the contributions of each MWNT to the field-emission pattern to be easily distinguished.

The researchers determined the temperature and resistance from TEDs obtained for various I_{FE}. As I_{FE} increased, the TEDs became broader and shifted to lower energy. The broadening is partly explained by the rise in the temperature due to Joule heating along the MWNTs. The shift to lower energy results from an IR drop along the tube.

ELIZABETH SHACK

Carbon Nanotube Bandgaps Manipulated with Metallofullerenes

A team of researchers from Seoul National University, Soongsil University, and Nagoya University has detected localized bandgap-energy changes in single-walled carbon nanotubes (SWNTs) that contain fullerene (C_{82}) encapsulated gadolinium ions (GdMF). As reported in the February 28 issue of *Nature*, research led by Young Kuk from Seoul National University demonstrated that bandgap energies of single SWNTs were tailored with ~3-nm accuracy using GdMF insertion to induce changes in nanotube structure and electronic environment and divide the nanotube into multiple quantum dots. Scanning tunneling microscopy (STM) was employed to monitor changes in tunneling conductivity to probe for breaks in symmetry imposed on the SWNTs. The major motivation is the development of nanoscale electronic devices as alternatives to Si-based devices.

The metallofullerene insertion into SWNTs was accomplished by heating the two in a glass ampoule at 500°C for three days. The diameters of the GdMF inserted were slightly larger than the SWNTs and could be spaced in a systematic fashion (every 1.1 nm) or quasi-periodically (every 1–3 nm), depending upon either a sonication or annealing method. The GdMF and SWNTs were both fabricated by a dc arc-discharge method, with the GdMF purified through high-performance liquid chromatography, and SWNTs purified by treatment with acid.

Using STM operated at ~5 K, dI/dV spectra were obtained from the images to estimate the bandgap at 512 points along a 10-nm section of a single SWNT. In areas that did not contain GdMF density, the SWNTs had a bandgap of 0.43 eV, while in the areas of GdMF insertion, the bandgap decreased to 0.17 eV. The evidence for such changes in tunneling conductivity along single SWNTs could be easily seen in the STM images, with bright "spots" appearing in a periodic fashion. Such bright spots are likely to be from both bandgap change and also topography change. The researchers believe insertion of GdMF into SWNTs has two effects along this line. First, the electron transfer from both the Au(111) substrate and the GdMF cluster may lead to charge transfers, resulting in the bandgap change. Second, the insertion of a GdMF with a greater diameter than the SWNTs introduces an elastic strain of the SWNTs, contributing to additional bandgap change.

The researchers believe that this ability to transform a SWNT into a one-dimensional multiple-quantum-dot system may contribute to the fields of nanoelectronics, nano-optoelectronics, and perhaps even a quantum cascade laser or quantum computer.

MATHEW M. MAYE

Computational Technique Facilitates Modeling of Fluid Transport in Porous Media

Computational materials scientist Clint Van Siclen, from the Idaho National Engineering and Environmental Laboratory, has demonstrated a theoretical approach to modeling fluid transport in porous, variable materials such as rock. Through his approach, called the walker diffusion method (WDM), Van Siclen calculates how electricity "diffuses" through a composite material. The WDM is based on the concept of a single random walker—a theoretical construct that "walks" through the material, randomly taking a step in one direction, a step in another direction, and so on. Left alone long enough, the walker will eventually explore all the potential paths available. By tracking these paths, Van Siclen is able to map out the fluid-flow routes in a permeable material, including sharp twists and turns or the tiniest of crack lines.

As reported in the February issue of *Physical Review E*, Van Siclen maps out the movements of the walker by first digitizing the structure of the porous material. That digitized representation is thus a square or cubic array of pixels or voxels, each of which is open or closed, corresponding to pore space and impermeable rock, respectively. If a pixel is open, there is a high probability that a walker will travel through that space. If the pixel is closed, then a walker will not be able to occupy that space. In a relatively short period of time, a walker can explore the accessible space using these simple, quickly computed probabilities. The calculations go even faster if several non-interacting walkers are used. These paths reveal the overall physical structure of the material.

With the conventional approach to calculating flow paths, called the finite-difference method (FDM), researchers take the digitized sample and construct a very large set of finite-difference equations, that is, equations that define the difference between the values of a function at two discrete points. Those equations have to be solved simultaneously, a task that strains the capabilities of all but the largest computers for realistically sized systems. In contrast, the WDM can be performed on a typical PC.

Furthermore, Van Siclen reports, the WDM obtains the "correlation length" for the material under study. This parameter is the size above which a specimen is uniform (homogeneous) with respect to the transport property of interest, such as fluid permeability, and below which it is variable (heterogeneous). The existence of the correlation length, which may be tens or hundreds of meters in the case of fractured bedrock, thus fundamentally limits the extent to which results from laboratory experiments are applicable to field sites.

According to Van Siclen, the WDM enables very large, or highly resolved,

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materials systems to be studied. Currently, the WDM is used as a research tool to determine relationships between the geological structure of the subsurface and fluid-flow phenomena. For example, it produces the correct dynamics of the displacement of one fluid by another, such as oil by brine in an oil reservoir, and groundwater by heavier-than-water contaminants in an aquifer. WDM has also been used to predict the thermal properties of new composite materials proposed for use in nuclear reactors. Theoretical mathematical research such as Van Siclen's work aids in the development of accurate and reliable predictive models.

Switching and Memory Effects due to CDW Deformation Observed in $K_{0.3}MoO_3$

Sliding charge-density-wave (CDW) materials exhibit unique memory effects including pulse sign memory, pulse duration memory, and delayed conduction. CDW materials are composed of an elastic periodic medium under the influence of randomly distributed pinning sites. Under an external driving force, CDW materials show a dynamic phase transition from a creep phase to a slide phase. A strong nonlinear conduction, called switching, corresponds to this transition. As reported in the April 29 issue of *Applied Physics Letters*, N. Ogawa and K. Miyano of the University of Tokyo have demonstrated electro-optical switch and memory effects in $K_{0.3}MoO_3$, a CDW material. The researchers established this CDW material as an electrically writable/readable and optically erasable memory device by incorporating only two electrical leads.

The researchers demonstrated optical switching in $K_{0.3}MoO_3$ by applying an increasing voltage and light illumination to a sample at 12 K. Below the sliding voltage, V_s, the current in the sample was caused by the creeping motion of the CDW. At V_s, the current in the sample increased by about 3 orders of magnitude. According to the researchers, this observed switching at V_s corresponds to the creep-to-slide dynamic phase transition. The creep current and V_s increase with increasing light illumination, an indication of optical excitation affecting the dynamic phase transition of the CDW.

The researchers also demonstrate conduction delay of the CDW transport. Application of a voltage slightly larger than V_s and a rectangular voltage pulse causes, after a time delay, sliding motion of the CDW. By illuminating the sample before the voltage pulse, there is an increase in the time delay. The delay time depends on the amplitude of the voltage pulse and the illumination intensity. After the initial sliding effect, sliding occurs more quickly when the next voltage step is applied. This is the memory effect.

According to the researchers, these results indicate that the CDW dynamic phase transition from creep phase to slide phase can be set by an external electric field and removed by photoexcitation and that this property can be exploited to realize an electrically readable switch or memory device.

JENNIFER BURRIS

Low Humidity Content in Soil Detected Using an Indium-Doped Tin Oxide (ITO) Sensor

Agriculture is not immune to the current global trend of reducing costs to increase profitability. Automatic irrigation systems are currently available to help reach this goal. Some of these systems operate within a scheduled time frame, and others work by controlling the amount of water present in the soil, allowing watering only when it is needed and thus compensating for unexpected changes in weather. The latter can be achieved by using sensors embedded in the soil.

Sensors used to monitor the water content in the soil measure either dielectric permittivity or electrical resistance. Sensors that measure dielectric permittivity are expensive though more reliable, and are typically used for higher water content measurements. Sensors that measure electrical resistance typically measure atmospheric moisture. These are porous materials in which surface adsorption of water molecules in the internal cavities changes the conductivity; therefore, the harshness of the environment determines the capability for monitoring humidity in the soil after long periods of time.

A group of scientists from the Universitat Jaume I in Spain have attempted to develop an inexpensive sensor to provide accurate measurements at low humidity levels in the soil. Their first steps toward developing such a device from indium-doped tin oxide (ITO) are described in the April 15 issue of *Applied Physics Letters*. ITO is a wide-bandgap semiconductor with high conductivity. The cost and availability, and chemical stability in water, basic, and acidic solutions, make ITO an excellent choice for this application.

Square pieces of glass (1.5 cm × 1.5 cm) coated with an ITO film served as electrodes, with a groove 500 µm wide dividing the film in half. Silver epoxy fixed the electrical contacts on each half, and a commercial thermoplastic was thermally sealed on top of each electrode. As a first test, this sensor was used to measure the humidity in 2 kg of soil placed inside a container. The scientists placed the sensor in contact with the soil itself, and then applied a voltage of 100 mV with sinusoidal amplitude. The ac impedance response obtained had considerable reproducibility at different conditions of dryness and humidity.

At low frequencies, the results show the effect of electrode polarization. At high frequencies, the bulk response results from the combination of a resistance R_p and a capacitance C_p, in parallel. These two values, resolved by the appropriate software, varied with the water content in the soil. The resistance R_p decreased about 2 orders of magnitude with an increase in the water content from ~3 wt% to 10 wt%; the capacitance Cp increased from 1.2×10^{-10} F to 1.8×10^{-10} F from driest to water-saturated soil. Since the capacitance is negligible as compared with the values for surface polarization at the Helmholtz layer, ~5 µF/cm^2, these observations cannot be attributed to a contact effect, said the researchers.

F. Fabregat-Santiago and co-workers said the behavior of the ITO sensor in terms of the two adsorption mechanisms represents chemical adsorption, where the electrostatic field of surface ions attracts water molecules to form the first layer; and physical adsorption, where water molecules dissociate and release protons to form additional layers. In these two cases and at low-humidity levels, the released protons determine the nature of the electrical conductivity. At high humidity levels, water condenses and then electrolytic conduction also contributes to the electrical conductivity. For this reason, a plateau in the conductivity appears at humidity levels of 10% and higher, according to the researchers. This trend is consistent with measurements conducted in different conditions; in some cases, the value of the resistance increased as expected when the dielectric constant of the medium increased, but the trend remained the same.

The ITO sensor can accurately detect low levels of humidity in the soil, and it addresses the main concerns of cost and reliability of measurements at low humidity. However, the researchers said that further testing is needed under operational conditions in the field to determine the applicability of this device for triggering an automatic irrigation system during extended periods of time.

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