Low-Temperature AFM Reveals Hidden Atom in Graphite Surface

The existence of atoms was hotly debated by leading scientists only 100 years ago. While field ion microscopy was the first technique to image individual atoms, scanning tunneling electron microscopy (STM) is now routinely used to observe single atoms in real space on flat surfaces. However, a classic problem is the "missing" atoms in the surface of graphite; that is, the three atoms (α) in the hexagonal lattice bonded to subsurface atoms have less electron density at the Fermi level than the three atoms (β) lying above holes. Because STM only probes the mobile electrons that cause the electric conductivity—that is, the electrons with an energy close to the Fermi level—only β atoms appear in STM images. Although atomic force microscopy (AFM) should in principle be able to image all surface atoms, previous AFM images showed only a single protrusion per unit cell. Recently, however, S. Hembacher, F.J. Giessibl, and J. Mannhart of Universität Augsburg, Germany, and C.F. Quate of Stanford University have shown that the missing surface atoms in graphite are observable with an AFM capable of detecting very small repulsive forces between single atoms.

As reported in the October 28, 2003 issue of the *Proceedings of the National Academy of Sciences*, the researchers combined STM and AFM at low temperature to simultaneously record the tunneling current and short-range forces to probe the charge density at the Fermi level and the total charge density, respectively, of graphite. Built on a 30-ton foundation to damp external vibrations and immersed in a liquid He bath cryostat, the combined STM-AFM operates in an ultrahigh vacuum with a sample temperature of 4.89 K. The frequency modulation force microscopy method makes possible combined STM-AFM experiments. The simultaneous measurement of current and force allows the research team to rule out double tip effects that probably have caused the sporadic previous observations of the full hexagon in STM or AFM experiments. The researchers had previously achieved subatomic resolution with this technique and imaged structures related to atomic orbitals.

The researchers said that because the layers in graphite are only weakly coupled, the normal forces between the AFM tip and the sample must be kept extremely small in order to avoid distorting the graphite lattice. The tungsten tip was shaped by field emission and controlled collisions until topographic images with corrugation of only 20 pm were obtained. Whereas an STM image recorded in constant-height mode shows only the β atoms, both types of atoms are imaged when the frequency-shift data are recorded simultaneously, that is, with the STM-AFM. The researchers attribute the short-range forces acting between the tip and the sample, indicated by the positive frequency shifts, to overlap of the 5*s*-, 5*p*-, and 6*s*-like orbitals of the tungsten tip with the sample orbitals.

Giessibl and co-workers have demonstrated an additional capability of AFM to gather information on surfaces that are only partially accessible by STM. They believe that "the successful imaging of the complete surface lattice of graphite is an important milestone for the imaging of other soft materials, [including] insulating organic molecules, with atomic resolution."

STEVEN TROHALAKI

Pyroelectric Effects Observed in Amorphous $BaTiO_3$

The pyroelectric effect, in which a temperature change is accompanied by a change in the polarization state of a material, is usually associated with polar crystalline solids. Recent research has focused on size effects, or the reduction of material response at nanometer-size length scales, that may limit device applications. In studying the size limits of crystallites yielding the desired material response, it is interesting to consider whether or not pyroelectric behavior can be observed in noncrystalline materials. In fact, all that is necessary for the manifestation of a pyroelectric response is directionally ordered polar molecules. This can in principle be achieved in a liquid, as evidenced in nematic liquid crystals, as well as in ionic solids. What is needed is a driving force for forming, and then ordering, the polar regions. V. Lyahovitskaya of the Department of Materials and Interfaces at the Weizmann Institute of Science in Israel and co-workers at the Weizmann Institute and the Swiss Federal Institute of Technology have recently produced quasi-amorphous (<0.3% crystallinity) solid $BaTiO_3$ exhibiting pyroelectric coefficients of 10–30 $\mu C/m^2$ V (5–15% of single-crystal values). This work demonstrates the feasibility of producing materials that are pyroelectric while retaining their amorphous character, as evidenced by x-ray diffraction (XRD) and transmission electron microscopy (TEM).

As reported in the November 2003 issue of *Advanced Materials*, pyroelectrically active $BaTiO_3$ films were obtained by passing as-deposited (rf-sputtered) $BaTiO_3$ films on doped Si(100) substrates through a steep temperature gradient. The as-deposited films gave no pyroelectric signal and possessed a temperature-independent low dielectric constant of ~9, while the films that passed through the temperature gradient displayed pyroelectric coefficients of 10–30 $\mu C/m^2$ K, and an increased but essentially temperature- and frequency-independent dielectric constant of 33 with low loss levels of 0.02. The increase in dielectric constant is consistent with the ordering of crystal motifs. The sign or magnitude of the pyroelectric response did not change after application of a poling field of 200 kV/cm, which indicates a fixed direction of polarization. The researchers reported that additional heat treatments through a temperature gradient, as well as isothermal heating, also did not affect the pyroelectric properties. In addition, films that were passed through the steep temperature gradient displayed piezoelectric activity with d_{33} values of 10 pm/V (5–10% of single crystal values). Crystallites were rarely detected by TEM investigations and absent from the XRD spectra, and the concentrations were estimated to be well below 0.3%. Therefore, the observed pyroelectric and piezoelectric activities of up to 15% of single-crystal values were attributed to the gradient of the strain-induced directional polar state.

KYLE BRINKMAN

Daylight Photocatalysis Achieved on Carbon-Doped TiO_2

The evidence of photoelectrochemical splitting of H_2O over TiO_2 to form OH radicals by Fujishima and Honda in 1972 initiated a great deal of research activity continuing to the present time. However, the industrial application of titanium dioxide in photocatalysis is still limited because of the large energy bandgap of TiO_2 (3.20 eV) that results in absorbance of only a small UV fraction of solar light (about 2–3%). Nonetheless, S. Sakthivel and H. Kisch from the Institute of Inorganic Chemistry of Erlangen-Nürnberg University, Germany, have recently achieved a significant photodegradation of water pollutants by daylight excitation of carbon-modified titanium dioxide.

As reported in the October 20, 2003 issue of *Angewandte Chemie*, the researchers synthesized carbon-doped TiO_2 by hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcinations in the air. This method leads to the formation of anatase-based compounds that contain residual carbon instead of nitrogen. The researchers determined the band structure of the materials and found the presence of surface states close to the valence-band

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edge. The presence of such states results in a trapped electron potential of –0.39 V, which exceeds the reduction potential of the O_2/O_2^- at pH 7 (–0.16 V), and enables the formation of OH radicals by visible-light irradiation.

The researchers, therefore, analyzed the photocatalytic activity of new materials by observing the degradation of typical pollutants in water and air by artificial and natural light. They observed complete photomineralization of the ubiquitous water pollutant 4-chlorophenol in the presence of the catalyst after 180 min of irradiation with visible light (λ = 455 nm). The researchers also confirmed high photocatalytic activity of the substances by photodegradation of 4-chlorophenol and the azo dye remazol red by illumination experiments in diffused indoor daylight. Furthermore, they found that the catalyst supported on filter paper catalyzes the oxidation of gaseous acetaldehyde, benzene, and carbon monoxide.

ANDREI A. ELISEEV

Micromirrors Fabricated by the Micro-Origami Technique Characterized by Optical Actuation

The development of semiconductors goes hand in hand with research into microelectromechanical systems (MEMS) devices because the latter, in a lot of cases, are built on semiconductors and consequently the progress of semiconductor research depends on the study of micro technologies. J.M. Zanardi Ocampo from ATR Laboratories in Kyoto, T. Ohnishi from Konan University in Kobe, R. Izumoto from Osaka City University in Osaka, and their colleagues addressed the formation of reliable hinges for movable parts of MEMS equipment, by means of micromirrors, and the actuation of the resulting micromirrors. As reported in the November 3, 2003, issue of *Applied Physics Letters*, the researchers have fabricated standing micromirrors by the micro-origami technique they developed in which the hinges bend as the result of strain in a pair of lattice-mismatched epitaxial layers. They then characterized the micromirrors by way of optical actuation.

To form the mirrors, the researchers used GaAs(100) as a substrate, $Al_{0.5}Ga_{0.5}As$/AlAs (40 nm) as a sacrificial layer, and $In_{0.22}Ga_{0.78}As$ (56 nm) as a strain layer, followed by a GaAs (88 nm) spacer layer. On top of that, they grew the mirror plate. They then processed the samples by photolithography and wet etching. Etching was selectively applied first to the component layer, then to all layers down to the etching stop layer and finally to the sacrificial layer. Powered by the strain relaxation of the InGaAs layer, the mirror stands by itself.

An Ar laser beam was focused on the surface to perform actuation of the mirrors. A HeNe laser probe beam was also focused on the mirror's surface and reflected onto a target placed several hundreds of millimeters away from the sample. This image was processed to analyze the mechanical response of the mirror during actuation. When the mirror was irradiated with the Ar laser, the HeNe probe light indicated a deflection in its inclination, which was positive. After the Ar laser optical excitation was interrupted, the mirror returned to its original angle. Thus, the frequency response of these mirrors was studied by applying a modulated optical excitation.

In order to explain this optical actuation, the researchers considered several phenomena. Light radiation pressure would not account for an increase in the mirror's inclination angle, as was found here, but rather a decrease. Actuation by heating and expansion of the surrounding air cannot be the reason because the mirrors move in vacuum as well. Stress by carrier generation remains a possible cause but short surface recombination times in GaAs and thinning of the epitaxial films can impede the actuation. As the researchers report, the most reasonable explanation could be uneven thermal expansion within the materials and thus deformation of the structures.

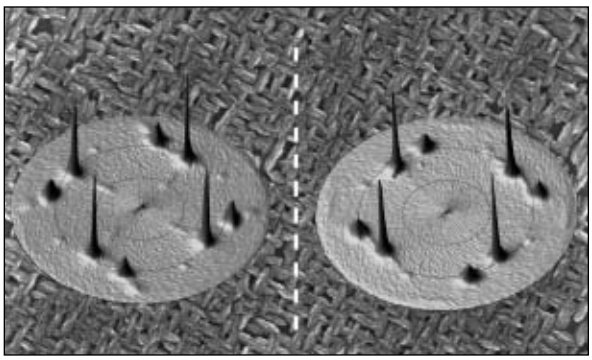
EKATERINA A. LITVINOVA

Chiral Surface Produced through Electrodeposition

J.A. Switzer and colleagues at the University of Missouri—Rolla have developed a process for separating or detecting chiral molecules using electrodeposited chiral surfaces, in contrast to the current process that requires a homogeneous catalyst or an enzyme solution. The electrodeposited chiral surface can then be used as this type of catalyst.

As reported in the October 2, 2003 issue of *Nature*, the researchers immersed a thin layer of gold in a liquid containing copper and the enantiospecific chemical tartrate while applying an electric current to the system. The electricity caused copper oxide to bond to the achiral Au(001) surface. The chirality of the film was determined by the chirality of the tartrate ion in solution. The researchers used x-ray diffraction to determine the orientation of the entire film, and x-ray pole figure analysis to determine the film's absolute configuration (see figure). Initial tests revealed that the material differentiates the enantiomeric forms of the chiral tartrate without breaking down or being permanently altered.

Switzer said, "We've made a material where the entire product is chiral, not just the surface. In earlier experiments, you would modify a surface with a chiral modifying agent, and if the agent washes off, the surface is no longer effective. In our research, the film itself is chiral, so the effectiveness remains even after many chemical reactions."



X-ray pole figures of ~300 nm CuO films electrodeposited onto a Au(001) surface. The background is a scanning electron microscope image of one of the CuO films. The pole figures—which represent data, not images of molecules—were created by use of an x-ray diffractometer.

Switzer said that the production of chiral surfaces is significant for the synthesis and detection of chiral molecules such as pharmaceuticals.

Photosensitive Membrane Fabricated by Molecular Imprinting

Molecular imprinting technology is an emerging method for the preparation of synthetic materials that use molecular recognition for selective separation and chemical identification. To prepare molecularly imprinted polymers (MIPs), a functional monomer and a cross-linker are polymerized in the presence of a template molecule. The template is then extracted, leaving cavities that are complementary in both shape and chemical functionality

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