

polarization-resolved mode and Fabry–Perot oscillations in a reflection geometry with a Fourier transform IR setup. The variation of the refractive index in this setup is found to be six to seven orders of magnitude higher than in bulk Si lattice. To verify that the birefringence of the anisotropically nanostructured Si layers has a dielectric nature and is not induced by stress, the pores of the samples were inundated with various dielectric liquids, and the ratio of the perpendicularly polarized light to the parallel polarized light was measured. The researchers found that the result supported the dielectric explanation of the birefringence in anisotropically nanostructured Si layers.

CLAUDIU MUNTELE

Soft Chemistry Method Developed for Synthesis of Cubic Boron Nitride

A team of researchers from Shandong and Beijing Science and Technology Universities and the Chinese Academy of Science have synthesized cubic boron nitride (cBN) at low temperatures and low pressures. As reported in the August issue of *Chemistry of Materials*, they used a solvothermal method to obtain nanocrystalline powders.

Cubic boron nitride is an attractive material for many applications due to its hardness, high thermal conductivity, and high-temperature stability. Unfortunately, the conventional synthesis of cBN from hexagonal BN requires extremely high temperatures and pressures (1200–2000°C and 2.5–7.5 GPa), which limits the possible batch sizes.

“But theory predicts that cBN should be stable at temperatures below 1300 K and pressures below 2 GPa,” said D.L. Cui, a professor at Shandong University. So his group investigated soft chemistry methods for the low-temperature and low-pressure synthesis of cBN.

Their process utilizes an anion exchange reaction between BBr_3 and Li_3N , using benzene as a solvent. The mixtures were heated for 8–12 h in a stainless steel autoclave at 480°C. The product was filtered, washed with water to remove the LiBr, and dried under vacuum at 80°C.

Transmission electron microscopy showed particles of nearly cuboidal shape and sizes of ~30 nm. Characterization by x-ray and electron diffraction and Fourier transformation IR spectroscopy revealed that the samples consisted of a mixture of different BN phases, with the cubic phase as the major one. Some hexagonal and orthorhombic BN were observed along with the cBN. The extracted lattice constants were in good agreement with liter-

ature values. The sample stoichiometry of B:N was confirmed by x-ray photoelectron spectroscopy. No oxide impurities could be detected.

Graduate student X.P. Hao said, “We are still trying to improve our synthetic methods. By now, we can prepare almost pure cBN at even lower temperatures, around 200°C, and pressures of 0.3–0.5 MPa.”

CORA LIND

Resorcinarene Promotes Self-Assembled Arrays of 2D Gold Nanoparticles

Chemists from Purdue University have developed a macrocyclic surfactant that enables gold nanoparticles in the mid-nanometer-size (10–200 nm) range to self-assemble into two-dimensional (2D) hexagonal close-packed arrays. As reported in the August 15 issue of the *Journal of the American Chemical Society*, the work demonstrates that particles as large as 170 nm can be dispersed at the air-water interface and organized into well-ordered monolayers when coated with resorcinarenes, a macrocycle with several hydrocarbon chains.

“Many nanostructured materials with mid-nanometer length scales have useful optical or magnetic properties, but are difficult to work with because of strong interparticle forces,” said researcher Alexander Wei, an assistant professor in the Department of Chemistry. “The resorcinarenes provide us with greater synthetic control for harnessing these materials into periodic structures with size-tunable properties.”

Wei’s research group has illustrated this point by measuring the arrays’ optical extinction properties, which were shown to vary dramatically as a function of periodicity. The arrays also exhibit strong and size-tunable surface-enhanced Raman scattering (SERS), the details of which will be published in *ChemPhysChem* later this year. The researchers are currently investigating the arrays for their potential as chemical sensors.

YUE HU

Organic LED Utilizes Flrpic for Efficient Blue Electrophosphorescence

A research team led by S. Forrest at The Center for Photonics and Optoelectronic Materials (POEM) at Princeton University has engineered an organic thin-film light-emitting device that will emit blue light using endothermic instead of conventional exothermic energy transfer. In order to create the energy transfer, the researchers used a 4,4'-N,N'-dicarbazole-biphenyl (CBP) conductive host

molecule doped with iridium(III)bis(4,6-difluorophenyl)pyridinato-N,C^{2'})picolinate, Flrpic. The researchers report in the September 3 issue of *Applied Physics Letters* that, “[t]o our knowledge, this is the first report of efficient blue electrophosphorescence.”

Although the researchers had prior success with red and green electrophosphorescent devices, they encountered a materials selection challenge due to the higher energy requirements of blue electrophosphorescence. Typically, the electrophosphorescence occurs when an exciton moves from a high energy state of the host molecule to a lower energy state on the phosphor, giving up energy in the process. However, the energy difference between the preferred host molecule and blue phosphors is not sufficient for luminescence via this conventional exothermic energy transfer. When investigating other potential host molecules, they found that a potential dichotomy existed between host materials with suitable high energy triplet states and host materials with appropriate energy level alignments with the other materials in the organic light-emitting devices (OLEDs). Consequently, the researchers pursued endothermic energy transfer in which the combination of applied current and existing thermal energy pushes excitons from the host molecule to the phosphor. They likely would not have achieved the same results without using a host molecule characterized by a very slow decay of its exciton.

The researchers grew OLEDs on a glass substrate precoated with a ~130-nm thick indium-tin-oxide (ITO) layer. Using a degreased and UV-ozone ambient cleaned glass/ITO substrate, the researchers grew the organic and metal cathode layers without breaking vacuum using an *in vacuo* mask exchange mechanism. After depositing the organic and metal cathode layers, the researchers encapsulated the device using a UV-epoxy resin under a nitrogen atmosphere. When describing the process, the researchers noted that, “[m]aintaining vacuum throughout the entire process is critical to attain high efficiencies.”

The researchers were able to achieve high photoluminescent efficiencies in several materials. However, to achieve the blue emission they sought, they had to introduce fluorine atoms and replace one of the ligands. Although the blue light emitted is not yet an exact match to the National Television Standards Committee (NTSC)-recommended blue for use in video displays, their ability to achieve wavelength shifts by creatively interchanging materials indicates that this material has the potential for an exact

match to the NTSC-recommended blue. In the mean time, the researchers believe that they have found a material with a blue emission already suited for many other video display applications.

PAMELA JOHNSON

Dislocations in Copper Observed to Form Preferentially at Twin Grain Boundaries

A team of scientists from the University of Idaho, Washington State University, and the Idaho National Engineering and Environmental Laboratory (INEEL) has discovered that dislocations in metals tend to form at twin grain boundaries. The research team further reported that while grain size determines at what stress level a material begins to deform, it has little effect on the ultimate strength a material can attain through deformation processing.

As published in the June issue of *Acta Materialia*, the researchers created copper samples with a range of crystal sizes by first straining the samples to create a high density of imperfections, and then heat-treating the metal at different furnace temperatures. Different grain sizes developed during recrystallization, depending on both the temperature and the number of imperfections in the original material. The team then tensile tested the material—stretching it at room temperature and monitoring the load generated by the applied strain. Using high-magnification microscopy, they periodically analyzed the deformed microstructure of each sample for clues to the formation of dislocations, dislocation density, and dislocation behavior.

"This is a basic mechanism of dislocation behavior not previously reported," said John Flinn, adjunct professor with the University of Idaho and retired INEEL researcher.

This observation is a departure from conventionally accepted materials-science theory stating that dislocations can form within the crystal grain itself or at any grain boundary—not just primarily at twin grain boundaries. This is the crux of understanding the role grain size plays in material strength, the researchers said.

By observing when and where dislocations develop, the research team documented that grain size plays a role only when plastic deformation begins. Materials with very small grain size can remain elastic longer than materials with larger grain size, and it takes more strain and higher stress to cause dislocations to develop. However, after dislocations have developed, grain size makes little difference. The increasing resistance to further deformation (strengthening) as a function

of strain once plastic deformation was initiated was the same for materials of all grain sizes. The team analyzed samples with grain sizes ranging from 3 μm to 60 μm and found that strain-hardening from plastic deformation was completely independent of grain size.

"Once you exceed the elastic limit of a material, the deformation behavior of the metal and improvements in mechanical strength from hardening is controlled by the interaction of one dislocation with another and not through interactions with grain boundaries," said INEEL scientist Tom Lillo.

For this research, the team initially strained the copper samples to induce a very high density and uniform distribution of imperfections before heat treatment. The combination of a high number of imperfections and low heat treatment temperatures enabled the researchers to create a range of grain sizes for experimentation. Using the technique called equal channel angular extrusion (ECAE), metal was extruded through a die with an internal 90° corner, rotated, and re-extruded. ECAE was much more effective in creating a high density of twin grain boundaries during heat treatment and subsequent recrystallization than the traditional cold-rolling. With ECAE, the research team achieved a density of almost 50% twin grain boundaries.

Flinn said, "The challenge now will be learning how to use this knowledge to design new high-strength, light-weight alloys." Such knowledge, Flinn said, will also help researchers to develop techniques for fabricating metals into various geometric forms for industrial utilization.

Silicone Polymer Scaffolds Facilitate the Growth of Lifelike Cardiac Tissue

Researchers at the University of Illinois at Chicago (UIC) and Loyola University Medical Center have grown lifelike cardiac tissue for possible use in the scaffolding and repair of damaged heart cells. The researchers first built scaffolds made from silicone polymers, which enabled them to study the grooves, pegs, and bumps of heart tissue. They were also able to mechanically manipulate the surface of the scaffolds to mimic the pumping of heart cells.

In the final phase of the project, the researchers attached heart cells firmly to the silicone surfaces of the scaffolds so that the mechanical activity could be mimicked in the laboratory. Luke Hanley, associate professor of chemistry and bioengineering at UIC, applied a rf discharge plasma to form hydroxy groups on the surface, fol-

lowed by wet chemical reactions with amine-terminated silanes and maleimide cross-linkers to link polypeptides to the silicone surfaces, fusing the cells to facilitate growth into healthy tissue.

Brenda Russell, professor of physiology and biophysics at the UIC College of Medicine, said, "The cells... migrated, found a micro projection, or a peg, and attached to it. More than 90% of the cells attached to a peg and stayed attached when mechanically pulsed." She explained that this is mainly due to the vertical topography, not the material itself. However, Russell said that the polypeptides are also enhancing the cell binding to the surface, presumably by activation of integrin-based cell adhesion mechanisms.

Silane Shown to Adhere to Phosphate Glass Surface

Sodium aluminophosphate glasses, doped with rare-earth elements such as erbium and ytterbium, are used in optical and photonic systems as laser sources and as waveguide amplifiers. In order to combine glass with another material to create a composite, an intermediary polymer coupling agent can be used, typically the silane aminopropyltrethoxysilane (APS). At the 19th International Congress on Glass, Amy Barnes, a graduate student at The Pennsylvania State University, reported, "We have shown that we can get silane to adhere to phosphate glass surfaces. The coating can protect the surface, minimizing corrosion, or can be a mediator between the glass and a polymer." The conference was sponsored by the Society for Glass Technology in Edinburgh, Scotland, in the beginning of July.

The researchers at Penn State studied the phosphate glass without the rare-earth elements to see how the silane adhered to the surface of the phosphate glass. The glass was dipped in APS and rinsed to remove loosely bound molecules. The researchers found that the silane forms a single or multiple molecular layers on the glass surface. The acidity of the silane solution affects the coverage of the surface differently than on traditional silicate glasses. The researchers said that the stability of the bond that forms may be different if the surface corrodes during coating.

For silicates, the maximum amount of adsorbed silane is reported to occur when the solution pH is near the natural pH of the molecule (pH of 10.5). In contrast, the maximum amount of adsorbed silane on the multicomponent phosphate glass occurred at a solution pH ~7 and decreased with both increasing and decreasing