

of Central Florida, and their co-workers. As reported in the February issue of the *Journal of the American Ceramic Society* (p. 466, DOI: 10.1111/j.1551-2916.2005.00069.x), these nanostructures with rectangular cross sections and triangular tips result from high-temperature pyrolysis of polyureasilazane in the presence of an FeCl<sub>2</sub> catalyst and N<sub>2</sub> vapor.

A powder precursor formed by curing the polyureasilazane and ball-milling it with the catalyst material was annealed at 1450°C, yielding nanobelts 50–100 nm thick, 400–1000 nm wide, and ranging in length from hundreds of microns to several millimeters. Energy-dispersive spectrum analysis confirmed that the nanobelts consisted only of Si and N. High-resolution transmission electron microscopy revealed that the belts were perfectly crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> with both [011] and [100] growth directions. Investigation of the structure using x-ray diffraction verified the presence of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, and a broad underlying diffraction peak was interpreted to come from an amorphous precursor that remained under the nanobelts.

The researchers suggest a solid–liquid–gas–solid growth mechanism for the nanobelts. As the amorphous Si–C–N precursor is heated with the Fe catalyst, a Si–Fe–C liquid eutectic forms and becomes supersaturated with Si and C. The supersaturated liquid reacts with N<sub>2</sub> vapor to form stable Si<sub>3</sub>N<sub>4</sub> precipitates, which then grow into the nanowires. To account for the rectangular cross sections, the researchers propose that after the Si<sub>3</sub>N<sub>4</sub> nucleates within the liquid droplets, the precipitate grows anisotropically due to the nature of the nitride crystal structure. Once the base of the triangular precipitate is the same dimension as the eutectic drop, the width ceases to increase but growth continues along the axial direction. Since other studies have shown that round nanowires can be grown in similar materials systems but at lower temperatures, Yang and co-workers are currently examining a hypothesis that the lower solubility of Si in the eutectic phase at lower temperatures results in smaller droplets, which in turn limits anisotropic growth of the nitride precipitates.

AMANDA GIERMANN

### Doped PMMA Used For 3D Multilayered Optical Memory

As reported in the April 1 issue of *Optics Letters* (p. 774), H. Jiu and co-workers at the University of Science and Technology of China use a femtosecond-pulsed infrared laser to sequentially create eight layers of voids, with diameters less than a micrometer, within a block of

doped poly(methyl methacrylate) (PMMA). Their result joins a body of research that uses pulsed lasers to controllably form voids within dielectric and polymer materials. This activity has been prompted mainly by the allure of applications in microfabrication and high-density optical storage.

As a dopant, the researchers chose an easily synthesized rare-earth complex, Sm(DBM)<sub>3</sub>Phen, which is highly soluble in PMMA. Compared with pure PMMA, the doped polymer has a lower optical memory threshold, which is due to the strong absorption of DBM (dibenzoylmethane) at 400 nm. A high and uniform concentration of dopant compounds resulted in stability and reproducibility during the subsequent laser etching process.

The group members use a Ti:sapphire laser operating at 800 nm (in the infrared region) to create the embedded voids. Because the polymer is largely transparent at this wavelength, single photons penetrate easily to the desired void depth, tens of micrometers within the sample. Once inside the doped PMMA, the laser beam is focused, and multiphoton absorption then excites a micro-explosion that causes controlled damage to a tiny volume. Each pulse changes one region, or binary data bit, within the material. Electron spin resonance spectra of the sample, taken before and after the laser-induced damage, confirm the photodegradation of PMMA.

Jiu and co-workers then read out these bits, both serially by observing the fluorescence of the structurally altered cavities under illumination by a 514.5 nm argon laser, and also in parallel by imaging the region with a CCD coupled to an optical microscope. Fluorescence in the void regions is strongly enhanced, which the researchers attribute to defects introduced by the scission of bonds of PMMA.

“With our validation of how voids can be arranged and then also detected within this storage medium at room temperature,” said co-researcher Qijin Zhang, “we have demonstrated the basic parts of a 3D, multilayered, read-only optical memory system.”

RICHARD LOUIE

### Anthracene Derivatives Used to Form *n*- and *p*-Type OFETs

Organic semiconductors have been widely studied from the viewpoints of their fundamental optoelectronic properties and their potential applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells. Novel *p*- and *n*-type organic semiconductors can be produced by introducing electron-accepting or

electron-donating groups as terminal groups into a common core unit (e.g., thiophene oligomers). When the core units consist of acene, pentacene is known to exhibit the highest mobility ( $\mu = 3.0 \text{ cm}^2/\text{V s}$ ) among OFETs. However, poor solubility in common organic solvents and instability in air makes pentacene difficult to modify. S. Ando of the Tokyo Institute of Technology, E. Fujiwara of the Institute for Molecular Science, Y. Inoue of NHK Science and Technical Research Laboratories, and their colleagues have reported anthracene as a preferred candidate over pentacene for its better solubility. The researchers prepared two new anthracene derivatives as semiconductors for FETs to prove the effect of terminal groups on charge transport. The research team believes this is to be the first *n*-type performance of anthracene derivatives.

As reported in the March 22 issue of *Chemistry of Materials* (p. 1261; DOI: 10.1021/cm0478632), thiophene rings (1) and 4-trifluoromethylphenyl rings (2) are used as terminal groups for electron-donating and electron-accepting parts, respectively, in an anthracene unit to produce derivatives for *p*- and *n*-type transistor materials. The researchers constructed OFETs using these derivatives and demonstrated their performances as *p*- and *n*-type semiconductors. OFETs were fabricated on SiO<sub>2</sub>/Si substrates using a top-contact geometry with gold source and drain contacts deposited on the organics. According to the research team, the absorption data reveal that the HOMO–LUMO gap for 1 is 2.85 eV and 2.68 eV for 2. Through analysis, the researchers demonstrated that FETs with the derivatives 1 and 2 have been constructed with electron and hole mobilities on the order of 10<sup>-3</sup> cm<sup>2</sup>/V s. X-ray diffraction, they said, reveals high lamellar ordering and crystallinity for 1 and disorder for 2. Atomic force microscopy shows a small grain size for 1 and a large grain size for 2, which have important implications for transport. The researchers conclude that the terminal substituents near the gate electrode have a great effect in determining the polarity of FET characteristics.

VIVEK RANJAN

### Nanopipettes and Nanoparticles Enable Detection of Single DNA Molecules

Progress in DNA detection methods may lead to new ultrafast DNA sequencing methods, which are essential for the development of new lab-on-a-chip technologies. In the February issue of *Nano-Letters* (p. 403; DOI: 10.1021/nl0480464), M. Karhanek and colleagues from the

Stanford Genome Technology Center at Stanford University have introduced a process to detect and potentially identify single DNA molecules labeled with nanoscale gold particles. While other groups have tried to develop such screening technologies using nanopores, Karhanek and colleagues use nanopipettes combined with measurements of electrical activity. They have found that nanopipettes are faster, easier, and less expensive to fabricate than nanopores.

The nanopipettes were produced from standard quartz capillary tubes (inner diameter, 0.7 mm; outer diameter, 1.0 mm) that were pulled to a needle point with nanometer-scale openings at the point end. The pulling was accomplished with the aid of a laser-based pipette puller. The diameter of the opening of the nanopipette is ~50 nm.

The researchers attached gold particles to DNA molecules to facilitate detection. The 10-nm-diameter nanoparticles were prepared, stabilized with dipotassium bis(p-sulfonatophenyl) phenylphosphine, and bound to 24-mer oligonucleotides. Through a series of experiments, the research team focused on detecting ionic current blockade events caused by the DNA-gold particles flowing through the tip of the nanopipette. This was accomplished by placing the nanopipette, filled with a KCl solution and the nanoparticle-DNA colloid, into a bath containing the KCl solution. One Ag/AgCl electrode was placed in the bath as a reference, and another was placed into the wide end of the nanopipette in contact with the solution. The researchers then monitored changes in current flow between the two electrodes and observed current jumps (blockades) whenever the nanoparticle or the oligonucleotide blocked ionic transport through the opening in the nanopipette.

Based on a statistical analysis of the blockade events, the researchers were able to infer structural information of the DNA-gold particles as they flowed through the sensor, including detection of the putative head and tail of the particles. They also observed that the DNA-gold particle often enters the pipette without full translocation. From the experimental data, the researchers said conditions exist for a certain energy profile with energy wells and barriers, causing a trapping and slowing of the molecules during translocation.

Karhanek and his colleagues concluded that this detection technique may lead to new versatile methods not only for the detection and identification of DNA molecules, but also for the detection of protein targets. For this purpose, the nanopipette tip could be functionalized with a target's

conjugate, said Karhanek. Such experiments may shed light on different conformations of the protein-ligand complex. In more general terms, these techniques may be used to study the dynamics and interactions of various biomolecules with their environment. Not only would this be helpful for technological breakthroughs, said the researchers, but it may also help to understand fundamentals about biological processes.

MARKUS J. BUEHLER

### Novel Hexaferrites Show Potential for Microwave Applications

X. Wang and colleagues at Tsinghua University in Beijing have synthesized  $\text{Ba}_3\text{Co}_{2-x}\text{Zn}_x\text{Fe}_{24}\text{O}_{41}$  hexaferrites by the citrate precursor method to obtain a single Z-type phase structure without any secondary phase, with  $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0,$  and  $1.2$ . These hexaferrites can find applications in inductors in the microwave region and ultrahigh-frequency communications, as they display high permeability, high thermal stability, and a high cutoff frequency of ~2 GHz.

As reported in the February issue of the *Journal of the American Ceramic Society* (p.478; DOI: 10.1111/j.1551-2916.2005.00081.x), the researchers used x-ray diffraction to characterize the phase structures of the powders, measuring the specific saturation magnetization and coercive field strength of the powders. X-ray diffraction patterns revealed that the formation temperatures of Z-type phase for Zn-substituted  $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  were between 1150°C and 1200°C. The substitution of Co by Zn ions at tetrahedral sites was found to result in an increase in the specific saturation magnetization. The Curie temperature, determined by thermomagnetic measurements, decreases linearly with the composition, from 410°C for undoped  $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  to 382°C for the composition with  $x = 1.2$ .

The researchers said that  $\text{Ba}_3\text{Co}_{2-x}\text{Zn}_x\text{Fe}_{24}\text{O}_{41}$  has high thermal stability and exhibits excellent magnetic properties; permeability rises to 9.8 for  $x = 1.2$  from 4.3 for the undoped ( $x = 0$ ) samples, while the resistivity remains above  $10^9 \Omega \text{ cm}$  for samples sintered at 890°C for six hours. The researchers said that the low-temperature-sintered  $\text{Ba}_3\text{Co}_{2-x}\text{Zn}_x\text{Fe}_{24}\text{O}_{41}$  will be a good candidate as a ferromagnetic material for use in multilayer chip inductor and multilayer chip beads at high frequencies.

VIVEK RANJAN

### Nitroxide-Mediated Polymerization of Styrene Demonstrated in a Continuous Tubular Reactor

Nitroxide-mediated polymerization (NMP), atom transfer radical polymeriza-

tion, and reversible addition-fragmentation transfer polymerization are frequently used in controlled free-radical polymerization. Compared with conventional free-radical polymerization, controlled free-radical polymerization provides narrow molecular-weight polydispersity, block copolymers, and complex structures. In the February 21 issue of *Macromolecular Rapid Communications* (p. 221; DOI: 10.1002/marc.200400531), T.E. Enright and B. Keoshkerian of the Xerox Research Centre of Canada and M.F. Cunningham of Queen's University, Canada, reported polystyrene preparation by a nitroxide-mediated mini-emulsion polymerization in a continuous tubular reactor. They used this method not only to simplify the polymer's synthesis with controlled microstructure, but also to provide better temperature and pressure control during the reaction. In addition, said Cunningham, "industry has expressed concerns over having to pressurize a batch (tank) reactor to run NMP in mini-emulsion, as it is not a standard practice, and the existing equipment is not well-suited for pressurized operation. However, tubular reactors can easily accommodate the modest pressures required (~300 kPa) and would be less expensive than tank reactors."

In the NMP of styrene, bulk prepolymerization was performed in batch by mixing styrene with benzyl peroxide and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in a 2 l stainless-steel reactor. TEMPO was used as the nitroxide-mediating agent. After the reactor was heated up to 135°C and cooled to room temperature, the monomer-polymer (a low-conversion polystyrene oligomer) mixture was dispersed in the aqueous phase, which was a sodium dodecylbenzenesulfonate deionized water solution. Then the mixture went through a homogenizer under a pressure of 400–600 bar, and the mini-emulsion latex was formed. Upon filling with the latex at the desired feed rate, this continuous reaction was performed in a 167 m stainless-steel tube coil in a 135°C oil bath. A simultaneous batch reaction was also done for comparison.

In either continuous or batch reaction, a stable latex was formed with a volume mean particle size of  $164 \pm 61 \text{ nm}$  in the batch reactor and  $170 \pm 59 \text{ nm}$  in the continuous reactor. Upon calculation, the coagulum left in both reactors was less than 0.5 wt% of the overall polymer. Both reactions showed very similar kinetic behavior such as the reaction conversion and rate. The polymers were characterized by gel permeation chromatography. For the polymer obtained from the tubu-