

B. Kimball and M. Sennett, and co-workers report on the development of nanosphere lithography, which utilizes commercially available suspensions of monodisperse polystyrene (PS) nanospheres (1 μm , 0.5 μm , 0.25 μm , and 0.125 μm in diameter). The researchers applied several μL of suspension to a clean silicon wafer. After immersion in de-ionized water and modification of the surface tension with a dodecylsodiumsulfate solution, a large, highly ordered monolayer of nanospheres formed on the water surface. Draining the water deposited the monolayer onto the silicon surface—or onto the surface of virtually any sufficiently flat substrate. Both the uniform diffraction color and a fast Fourier transform analysis confirmed that the monolayer was essentially free of defects.

The researchers subsequently employed the nanosphere monolayer as a template for catalyst deposition—electron-beam evaporation of Ni—after which the PS nanospheres were chemically removed. Images made by atomic force microscopy and scanning electron microscopy (SEM) showed that the Ni dots formed a honeycomb pattern. The Ni dots can be annealed first or used directly to grow CNT arrays by hot-filament PECVD. In this work, aligned CNTs were grown using acetylene gas as the carbon source and ammonia gas as both the plasma enhancer and growth promoter.

The researchers note that SEM images show that the CNTs are not as straight as those synthesized previously, but feel confident that the quality will improve with better nanosphere removal and with more control of the CNT growth. The colorful appearance of CNT arrays due to diffraction demonstrates their high metallicity (low dielectric loss) and the high degree of ordering, said the researchers.

The researchers employed a general theory of light diffraction to demonstrate that their honeycomb arrays of CNTs should lead to a diffraction pattern with triangular symmetry. Triangular symmetry was observed in the diffraction patterns obtained by shining green and blue laser light perpendicular to the plane of the lattice. The research team said that the rotational symmetry of the patterns shows that the scattering nanotubes are circularly symmetric in the plane and that the small hexatic pattern distortion points to the possibility of misaligned crystalline macro regions. The researchers also demonstrated that the specific dependency of the spot intensity on their order is consistent with theory.

Citing previous work demonstrating 2D hexagonal bandgap structures, the researchers reasoned that they could employ previously published theoretical

results after proper dielectric-constant scaling, which implied that their honeycomb array of nanotubes should act as a 2D photonic-bandgap crystal with a bandgap of about 0.5 μm . While demonstration of the photonic bandgap in their nanotube arrays is in progress, the researchers believe they can obtain photonic bandgaps in the visible range. They also said that the nanotubes can be coated for better control of the photonic-crystal parameters or can be used as structural templates for nonmetallic photonic arrays.

STEVEN TROHALAKI

Controlled Growth of GaN Single-Crystal Nanowires Demonstrated

Gallium nitride (GaN) has been shown, over the past several years, to be an important optoelectronic material. Success in the growth of high-quality GaN thin films has led to the development of various devices including blue light-emitting diodes and laser diodes. Recently, efforts have also been directed toward producing nanowires of GaN, which could be important for nanoscale optoelectronic applications. However, it has been difficult to control the size and location of the nanowires. Now, a group from the University of Southern California including Chongwu Zhou, Song Han, and co-workers has demonstrated control of nanowire diameters, nanowire growth locations on a substrate, and nanowire orientation with respect to a substrate. This was achieved through the use of monodispersed gold clusters as catalysts, as reported in the February issue of the *Journal of Materials Research*.

The researchers first demonstrated the use of e-beam evaporated Au nanoparticle clusters as a catalyst for the growth of GaN nanowires. They used a chemical vapor deposition (CVD) technique using a pure Ga source and flowing NH_3 gas to grow the nanowires. The synthesis was found to be based on the vapor-liquid-solid (VLS) growth mechanism wherein the Ga vapor diffuses into the gold catalytic particles, grows out, and reacts with the NH_3 forming GaN after the Ga/Au alloy achieves supersaturation. The nanowires were found to be single crystals growing in the [100] direction with a wurtzite structure, with the diameter approximating the diameter of the catalytic gold particles.

The researchers then used gold nanoclusters with specific diameters of 10 nm, 20 nm, and 30 nm. In each case, the nanowire diameters were uniform. Measurements of a number of nanowires yielded Gaussian distributions of diameters with average diameters of 11.9 nm, 18.5 nm, and 28.1 nm, respectively. In a separate experiment, gold nanoclusters were deposited at

desired sites on a Si/SiO₂ substrate using standard e-beam lithography, which yielded islands of the catalyst as dictated by the pattern. GaN nanowires were observed to grow only on these islands. In addition, it was possible to control the yield of nanowires by controlling the concentration of the gold nanoparticles.

An a-plane sapphire substrate, which also has a wurtzite structure, was used to grow the nanowires in an attempt to grow vertical nanowires. There is a 13% lattice mismatch between the sapphire and the GaN nanowires. Au nanoclusters were deposited using a transmission electron microscope grid as the shadow mask. CVD growth yielded GaN nanowires on the areas with the Au nanoclusters, mostly growing in a vertical orientation with respect to the substrate. Some nanowires were found to grow in other directions as well, which was attributed to the 13% lattice mismatch.

This ability to grow GaN nanowires with well-defined diameters, at desired and specified sites, and by achieving a high degree of orientation control, is crucial if the nanowires are to be used for nanoscale electronic and optoelectronic devices.

GOPAL R. RAO

Ordered Sol-Gel Composites with Submicrometer Periodicity Obtained

The preparation of mesostructured materials with high orientation order is emerging as a new area of technological and scientific interest, in particular, due to their possible use in such fields as catalysis, chromatography, filtration, photonics, and lithography of mesostructured films. Kalaichelvi Saravanamuttu and Mark P. Andrews of McGill University, Canada, have found an approach for the synthesis of macroscopically aligned mesostructured materials by using a template-free, room-temperature sol-gel route. As reported in the January issue of *Chemistry of Materials*, the researchers performed the sol-gel processing of simple silicon and transition-metal alkoxides with acrylate substituents (e.g., commercially available alkoxy silane: 3-methacryloxypropyltrimethoxysilane), which forms networks with long-range, microstructural organization with 250 nm periodicity. The suggested approach involves photoinitiated free-radical polymerization of the olefin groups, which “locks” this organization into mechanically stable, optically clear monoliths. The researchers said that before organic polymerization, composites could be spin-cast as microstructured, bicontinuous thin films. Previous studies have assumed that room-temperature sol-gel processing without templates leads

only to amorphous networks. The researchers confirmed a well-defined, ordered mesostructure by scanning and transmission electron microscopy studies. They also found that the solid monoliths obtained in this way were transparent but birefringent when observed between crossed polarizers.

Saravanamuttu and Andrews proposed a model based on bicontinuous microemulsions to explain the unusual submicrometer periodicity of the composites. Microemulsions are ternary systems composed of organic, H₂O, and surfactant phases. The researchers said that in their system, a microemulsion forms upon generation of amphiphilic oligosiloxanes through condensation reactions of alkoxy-silanes. Because they possess relatively short organic chains, sterical limitations, and non-ionic head groups, these oligomers cannot form micellar structures. Instead, they are likely to self-assemble into minimal-energy, amphiphilic monolayers with low curvature and bending rigidity that occupy the interfaces between immiscible organic (alkoxysilane) and H₂O phases. According to the researchers, this could lead to a thermodynamically stable bicontinuous microemulsion in which the oligosiloxane monolayers partition organic and aqueous phases into discrete volumes. This microstructure could then be "frozen" by photopolymerization of the acrylate moieties, they said.

ANDREI A. ELISEEV

Phases of Surface-Parallel Molecules Discovered in Hg-Supported Langmuir Monolayers

Langmuir monolayers (LMs) are formed by amphiphilic molecules like alcohols and fatty acids on a liquid surface. The structure and properties of these monolayers strongly depend on the architecture of the constituent molecules and their inter- and intramolecular interactions. Until recently, however, LMs were studied on aqueous subphases, where the hydrophobic repulsion aligns the molecules normal to the surface. In the November 15 issue of *Science*, researchers from Bar-Ilan University, Israel; Brookhaven National Laboratory; and Harvard University have reported angstrom resolution x-ray measurements of the coverage dependence of the structure of LMs formed by stearic acid on a liquid Hg subphase.

M. Deutsch of Bar-Ilan and co-workers said that the resolution is possible because the high surface tension of Hg results in a very low surface roughness (~1 Å). Under the combined action of the alkyl chain-Hg attraction and the weak but important carboxyl head group-Hg subphase bond (~1.5 kJ/mol), a small change in the coverage induces a drastic change in the orientation of the molecules relative to the surface. At high coverage, from 19.5 Å²/molecule to ~25 Å²/molecule, a monolayer showing two phases of surface-normal molecules was found, similar to those found on water. At low coverage, from 57 Å²/molecule to 120 Å²/molecule, two hitherto unobserved phases of single and double layers of surface-parallel molecules were found. These flat-lying phases consist of molecular dimers packed side by side to form stripes. Long-range in-plane order is found to exist in the direction normal to the stripes, but no order is found in the dimer ordering along the stripe. This one-dimensional order in a two-dimensional layer is, in effect, a two-dimensional smectic-like phase. X-ray reflectivity and grazing incidence diffraction were used for measuring the structure of the monolayer normal and parallel to the surface, respectively. Bragg rod measurements detected the molecular tilt magnitude and direction.

The researchers said that this understanding of the interactions is important in the emerging fields of nanofabrication and biometallic interfaces.

MAXIM NIKIFOROV

Single DNA Molecules Detected by Nanopore Technology

The development of nanopore-based biomolecule detection techniques has been impeded by the difficulty of nanopore manufacture and poor nanopore stability. Physics professor Lydia Sohn and graduate student Omar Saleh in the Department of Physics at Princeton University have described the microfabrication of a stable nanopore-sensing device achieved by well-established techniques. The device consists of two 5-µm-deep reservoirs connected by a 3-µm-long, 200-nm-diameter pore micro-molded into poly(dimethylsiloxane) (PDMS). The nanopore sensor detected single λ-phase DNA molecules by monitoring the electric current produced by the flow of analyte solution through the pore. The microfabrication procedure can also be

used to create sensors for proteins and peptides, as well as sensors that distinguish between different surface functionalities of an analyte molecule. According to Sohn, this nanopore-sensing device represents a "first step toward a host of single-molecule sensing applications."

As described in the January issue of *Nano Letters*, the researchers used electron-beam and photolithography techniques to pattern negative masters of the pore and reservoirs, respectively, as polystyrene structures onto a silica substrate. PDMS was then poured over the master and allowed to harden. The master was then removed and the PDMS slab sealed to a glass cover slip. The master for the mold is very durable and can be used to fabricate a large number of nanopore sensors, according to Sohn and Saleh.

Analyte solution was driven through the sensing nanopore by electrophoresis or by applying pressure to one of the reservoirs. The electric current that accompanied the flow was measured using platinum electrodes on the cover slip. The current through the pore was lower when a large molecule obstructed the flow of solvent. The drop in the current was proportional to the size of the molecule and allowed for coarse sizing of the DNA. The drop in the current was also lower for larger pores, and could not be reliably measured for pores >300 nm in diameter.

The researchers said that this device can be used to detect smaller biomolecules by reducing the pore size. They said the pore can also be functionalized with various molecular species to change the retention time, and current profile, of the analyte. This chemical interaction can also be used to distinguish between two similarly sized but differently functionalized analyte molecules, they said. The Sohn research group is currently investigating the manufacture of nanopore array devices for detection of multiple analytes, as well as devices that allow optical and electric screening of samples.

GREG KHITROV

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News of MRS Members/Materials Researchers

Ibon Azkona of the Basque Technology Centre has received an award from the **European Powder Metallurgy Association** for the **best European doctoral thesis on powder metallurgy in 2002**. The result

of the research carried out by Azkona has been the production of ultrahard materials based on transition-metal borides through a feasible route at industrial scale. The award was announced on October 8

during the EPMA conference held in Lausanne, Switzerland.

Camden R. Hubbard (Oak Ridge National Laboratory) has received the **2002 McMurdie Award** for contributions to the