



Figure. Crystal faces of hexagonal ZnO microrods and microtubes. Reprinted with permission from *Chem. Mater.*, December 17, 2001, **13**, 4395–4398. Copyright 2001 American Chemical Society.

Physical Chemistry at the University of Uppsala, Sweden, have prepared highly ordered arrays of hollow crystalline ZnO microtubes 1–2 μm in diameter and 10 μm in length. The preparation, carried out by Lionel Vayssieres and co-workers, consisted of the growth of oriented crystalline ZnO microrods by controlled precipitation of ZnO, and the selective etching of these rods to produce microtubes. The one-step synthesis was carried out in aqueous solution using common reagents and without the use of a template. This synthetic method allows for a simple, safe, and inexpensive production of *purpose-built* materials on a variety of substrates. According to the researchers, similar microrod arrays have demonstrated high-UV photoresponse and excellent electron-transfer properties with potential applications as catalysts, sensors, and other photovoltaic devices.

As reported in the December 17, 2001, issue of *Chemistry of Materials*, the researchers prepared the microtube arrays by thermal decomposition of a Zn^{2+} methenamine complex precursor in aqueous solution to produce ZnO. The arrays were grown on polycrystalline F-SnO₂ glass, silicon wafers, and indium-tin-oxide-coated polyester substrates. The substrates were covered with the precursor solution, and the reaction was kept at 90°C for two days. The precursor solution was prepared by dissolving $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and methenamine (both 0.1 M) in MilliQ + and water. Following the synthesis, the product materials were washed with water to remove any unreacted complex and salts. Microtube arrays covering several tens of square centimeters may be produced by this method.

The formation of the microtubes in the arrays exploits the chemical and structural metastability of the (001) face of the ZnO wurtzite structure. A ZnO microrod consists of a hexagonal single crystal elongated along the [001] direction (Figure, left). This elongation is the result of preferential growth of the (001) face during conditions of high precursor concentration on the first day of the synthesis. When the precursor concentration drops, the resultant Ostwald ripening, combined with the preferential dissolution of the (001) face, results in a net transfer of material from the (001) face to the more stable crystal faces, producing a hollow structure (Figure, right side).

Scanning electron microscopy of the product materials showed a uniform array of hexagonal microtubes 1–2 μm in diameter and 10 μm in length, oriented perpendicular to the substrate. X-ray and electron-diffraction studies confirm that the microtubes are crystalline and exhibit the wurtzite structure and lattice spacing of bulk ZnO. The crystallinity of the arrays allows the use of flexible and temperature-sensitive substrates by eliminating the need for high-temperature annealing normally required for materials grown at low temperatures.

GREG KHITROV

Array-to-Array Transfer of Microspheric Sensors Stable over Time

Researchers from Tufts University's Max Tishler Laboratory for Organic Chemistry and the Johns Hopkins University's Department of Mathematical Sciences have devised a method to manufacture artificial noses by using microsensors that are typically 3 μm in diameter. Due to the sensors' small size, literally billions of them can be made from the same feedstock. The microsensors are made of silica microspheres or polymer beads of variations of polystyrene. The microsensors are unique from other artificial-nose-array constituents in that they are relatively simple to make reproducibly, which allows for basically the same classifier training, an involved process typically done separately for each artificial nose array, to be used for all artificial-nose arrays made from the same baseline materials. The researchers said, "A conservative estimate puts the number of nose arrays made from 1 g of 3- μm feedstock at 10,000. Thus, we have essentially eliminated the need to retrain the classifier, thereby saving time and increasing accuracy."

As reported in the November 1, 2001, issue of *Analytical Chemistry*, the researchers led by David Walt at Tufts

University used 3- μm IB-Sil (C1), 3- μm Phenosphere (OH), 3- μm Luna (OH), and 5- μm Selectosil (SCX) silica microspheres; in addition to polymer beads of 3.12- μm P(S/55% divinylbenzene) and the copolymer PS802. The silica or polymer beads were first dipped in Nile red (a fluorescent indicator) and dyed in a batch process using fluorescent materials. Next, the sensors were placed in a vacuum-filtration system before being rinsed with toluene or chloroform to remove excess dye. In the final step, the researchers dried the sensors in a 100°C oven for ~1 h. The sensors were stored in the dark prior to use.

Once the dye process was complete, the researchers made a slurry of the five different bead/sphere types, which they then sandwiched between two glass cover slides. In addition to making these randomized arrays, the researchers also made five different arrays from each type of microsensor, in order to determine the characteristics of each. Using a fluorescence imaging system based upon a charge-coupled device camera, the nose arrays were tested for their ability to detect explosive nitroaromatic-compound (NAC) vapors in the presence of other volatile organic compounds (VOC). NAC vapor sources included 1,3-dinitrobenzene and 4-nitrotoluene. VOC vapor sources included acetone, benzene, chloroform, ethanol, ethyl acetate, heptane, methanol, toluene, and air carrier gas (control). Fluorescence was excited at 530 nm and monitored at 630 nm. Maps of sensor type were obtained by characterizing sensor interaction with air. Changes in fluorescence were then monitored for each sensor type upon exposure to other test samples. The researchers made many of the vapor mixtures overwhelmingly VOC, yet the artificial-nose arrays were almost always able to detect the NAC vapors. Indeed, the first artificial-nose array tested had a 98.2% correct classification rate, and the second nose array tested six months later had a 93.8% correct classification rate. Thus, these tests showed that the artificial-nose arrays produced using this scheme were not only accurate, but also stable over time.

PAMELA JOHNSON

A Particle Constrained in an Optical Trap Allows 3-D Imaging of Transparent Materials

Three-dimensional imaging of transparent materials can be achieved with a scanning probe microscope based on a dielectric particle trapped by optical tweezers. Its resolution is affected by thermal variations of the particle within the optical trap since the forces acting on this dielectrical particle are weaker than those

of soft scanning force microscope cantilevers. These cantilevers have oscillations perpendicular to the surface of the order of 10^{-10} m, while a particle in an optical trap can fluctuate as much as several hundred nanometers in any direction. In this manner, the particle is able to scan over an area becoming a "natural 3-D mechanism".

Scientists from the European Molecular Biology Laboratory in Germany obtained 3-D images of an agar gel by means of this technique, as they describe in the November 26, 2001, issue of *Applied Physics Letters*. An agar gel is a transparent substrate used for biological cultures and chromatography. In this case, liquid agar was mixed with latex beads with a nominal diameter of 216 ± 8 nm. The beads were added at a concentration of $1/20 \mu\text{m}^3$. A photonic force microscope, which is a scanning force microscope based on optical tweezers, was used to conduct the experiments. It included a 1064-nm laser beam and a three-dimensional detector. This detector consists of a quadrant photodiode where the scattered laser light from the particle produces an interference pattern. The position of the optical trap is measured with <1 nm error; the position of the center of the particle is measured with nanometer resolution.

A position histogram was calculated after recording the position of a particle for 0.8 s. The thermally induced particle fluctuations allowed it to scan a volume of $300 \times 120 \times 120 \text{ nm}^3$. It was also possible for the particle to scan areas around an object. When the optical trap was moved along the agar network in 80-nm steps, the variations on the position of the particle showed indications of the presence of the network filaments. The same effect was observed when the optical trap was moved along the x - and y -axes of the agar network in 80-nm steps and along the z -axis in 160 nm steps. After scanning a volume of $600 \times 600 \times 300 \text{ nm}^3$, three filaments of the agar network were detected: two of them located inside this volume and one at the edge. The size of the particle affects the resolution which, in these experiments, is ~ 20 nm.

SIARI S. SOSA

Micro-Optical Devices Dry Etched into Diamond

Diamond has the widest optical transparency window and highest thermal conductivity of all known substances. Consequently, it is a very versatile material for use in optics. Diffractive optical elements (DOEs) are interesting for many applications, including the shaping of CO_2 lasers and Nd:YAG lasers. As

reported in the November 15, 2001, issue of *Optics Letters*, M. Karlsson, K. Hjort, and F. Nikolajeff fabricated continuous-relief blazed gratings and diffractive Fresnel lenses in diamond of optical quality at the Angstrom Laboratory in Sweden. The DOE pattern was first written in an electron-sensitive resist by direct-write electron-beam lithography, then transferred from the resist into the diamond by dry-etching in an inductively coupled plasma. The researchers used electronic-grade O_2 and Ar gases for etching of the diamond substrate, and the surfaces were polished to a root-mean-square (rms) roughness of <15 nm.

The transfer of the DOEs from the electron-beam resist into diamond was made in an inductively coupled plasma (ICP) etching system. ICP etching is a high-density system with plasma-etch rates of 1900 nm/min in resist and 190 nm/min in diamond. The researchers reported that to their knowledge, this is the first time that dry etching has been used to transfer continuous structures into diamond. Both blazed gratings and diffractive Fresnel-type lenses were created. The transferred blazed grating was carefully inspected with both an optical microscope and with atomic-force microscopy (AFM) to measure the height of the structure, the surface morphology, and the accuracy of the transfer process. The blazed grating was found to have a period of 45 μm and a grating depth of 3 μm . By using AFM data from the original structure, researchers simulated a diffraction efficiency of 71.5% for the e-beam-exposed structure with a theoretical value of 100%. After etching, the final diamond structure had a diffraction efficiency in the first order of 68.2%, measured with a solid-state laser.

The group now intends to proceed with a more fundamental study of transferring micro-optical elements into diamond by using ICP etching. They also plan to fabricate diffractive and refractive elements for use with Nd:YAG high-power lasers. In this study, the researchers were unable to design optical elements for wavelengths larger than ~ 700 nm. However, they believe that replicating DOEs in photoresist might lead to optical elements for the infrared region, facilitating applications for 10.6- μm CO_2 lasers.

JENNIFER BURRIS

Reduction in Roughness of Waveguides Leads to Ultralow Transmission Loss

By reducing the sidewall roughness of Si/SiO₂ waveguides, researchers at the Massachusetts Institute of Technology and

the University of Wisconsin—Madison have achieved ultralow transmission losses of 0.8 dB/cm by using oxidation smoothing and anisotropic etching techniques. They believe this to be the smallest loss for a high-index-difference system reported to date.

Scattering losses in waveguides—as calculated by the commonly used method of Marcuse, Payne, and Lee—are proportional to the root-mean-square (rms) surface roughness. Typical rms roughness values for waveguides fabricated by conventional photolithography and reactive ion etching (RIE) techniques are about 10 nm, which yield scattering losses of about 32 dB/cm. By following the photolithography and RIE steps with wet oxidation smoothing or anisotropic etching, the researchers were able to reduce the sidewall roughness to 2 nm.

As reported in the December 1, 2001, issue of *Optics Letters*, K. Lee, D. Lim, and L. Kimerling at MIT, and J. Shin and F. Cerrina at Wisconsin first fabricated waveguides using standard methods. Starting with wafers consisting of a 0.2- μm -thick layer of Si on 1- μm -thick SiO₂, they patterned the surface using UV photolithography, and etched it with SF₆ gas. This produced straight waveguides with widths in the range of 0.5 μm –8 μm . For the oxidation-smoothing sample, the Si layer of the starting wafer was 0.34 μm thick. After photolithography and RIE, the waveguide core was subjected to wet oxidation by H₂O and O₂ at 1000°C for 43 min followed by an HF dip to remove the oxide.

The anisotropic-etching sample fabrication was more complicated. Again starting with a 0.34- μm -thick Si layer on a 1- μm -thick SiO₂ wafer, they oxidized the Si top layer to produce a 0.3- μm -thick SiO₂ layer on a 0.2- μm -thick Si core, leaving the 1- μm -thick Si base layer intact. The top SiO₂ layer was subject to photolithography and RIE to make a hard mask for the core of the waveguide, then the sample was immersed in a 25-wt% aqueous solution of NH₄OH at 80°C for 1 min to etch away the Si from the non-waveguide area. The oxide hard mask was removed, leaving a Si waveguide core.

Atomic force microscopy revealed rms surface roughness values of 2 nm for both the oxidation-smoothed and the anisotropically etched samples, versus 10 nm for the conventionally fabricated waveguide. Transmission-loss measurements versus waveguide width were performed using cutback, IR capture of scattered light, and Fabry–Perot resonance measurements. The reduced transmission loss due to smoother surfaces in the oxidation-