Ferromagnetism above Room Temperature Discovered in Mn-Doped ZnO

Ferromagnetism at and above room temperature in magnetic semiconductors is a property of significant interest for spintronic applications and devices. Mn-doped ZnO and GaN have been predicted, based on theoretical calculations, to be potential candidates for exhibiting ferromagnetism above room temperature, leading to an intense search for the right material. The first observations of ferromagnetism above room temperature for dilute Mn-doped ZnO have now been reported. K.V. Rao, P. Sharma, and their colleagues from the Royal Institute of Technology (Sweden) and from the Armament Research Center (United States), Arizona State University (United States), University of Uppsala (Sweden), and the University of Sheffield (United Kingdom) report this discovery in both bulk and thin transparent films of Mn-doped ZnO in the October issue of *Nature Materials*.

The incorporation of ferromagnetism in ZnO, a known piezoelectric and electro-optic material, may lead to various multifunctional properties. Doping ZnO with Mn, a 3*d* transition metal, can make possible the injection of a large amount of spins and carriers, making Mn-doped ZnO an excellent candidate for spintronic applications.

In this study, the material was made by mixing appropriate amounts of ZnO and MnO_2 powders. The powder mixture was then calcined at 400°C for 8 h and then sintered at temperatures ranging from 500°C to 900°C for 12 h to obtain $Zn_{1-x}Mn_xO$ (x = 0.01, 0.02, and 0.1). For samples sintered below 700°C, superconducting quantum interference device measurements revealed ferromagnetic ordering. Elemental mapping using electron dispersive spectroscopy showed that the Mn was uniformly distributed and the material was homogeneous with a single phase. Sintering the samples above 700°C suppressed the ferromagnetism to below room temperature. This was attributed to the formation of Mn clusters, which are antiferromagnetic, and/or the formation of other phases. Ferromagnetic resonance (FMR) measurements indicated that the 2 at.% Mn-doped ZnO is a ferromagnetic semiconductor with a Curie temperature T_c well above 425 K. The researchers said that this is likely the first FMR measurement of room-temperature ferromagnetism in a semiconductor.

Thin films of the $Zn_{1-x}Mn_xO$ were deposited on fused quartz substrates using a pulsed laser ablation technique. The films, which were transparent, also exhibited room-temperature ferromagnetism and phase homogeneity. High-resolution transmission electron microscopy on the thin films showed that the ZnO was ordered and oriented perpendicular to the *a–b* plane of a hexagonal lattice with a matching lattice parameter. The results suggest that the Mn substitutes for the Zn in the structure. This discovery of above-room-temperature ferromagnetism in Mn-doped ZnO semiconductors opens up a number of possibilities for spintronic applications and novel magneto-optical components.

GOPAL RAO

Large Diamond Crystals Grown at Low Temperatures

Synthetically made diamond is widely used for technological applications ranging from abrasives, tool coating, microelectronics, and optics to corrosion protection. Yet most techniques for making this material require high temperatures and pressures. Qianwang Chen, a professor of materials science and engineering at the University of Science and Technology of China, and his colleagues have made diamond crystals as large as 510 μm in size by reducing magnesium carbonate with sodium at temperatures as low as 500°C.

As reported in the September 29 issue of *Angewandte Chemie*, the researchers were able to carry out the reaction in an autoclave using autogenetic pressure. The preferential formation of diamond over graphite was found to be very sensitive to conditions of temperature, pressure, and starting concentration of reactants. The researchers think that magnesium carbonate is first pyrolyzed to yield the oxide and supercritical carbon dioxide. The latter is then reduced on the surfaces of molten sodium at high pressures to give the polyhedral diamond crystals, which are usually about 120 μm in length and can be as large as 510 μm. At 500°C and 860 atm pressure, reaction yields of up to 6.6% were attained. Raman spectroscopy and x-ray diffraction showed the formation of high-purity, well-crystallized diamond particles. Moreover, the researchers said, the diamond crystals are transparent and colorless. No diamond could be detected at process temperatures below 500°C.

Chen said, "It was in 1796 that it was shown that diamonds could be stoichiometrically converted to carbon dioxide by burning in oxygen, only now has it been possible to achieve the reverse conversion of dense carbon dioxide to large diamond crystals."

While the mechanism for carbonate reduction and diamond growth is not fully understood, the low cost of the starting materials and low temperatures used in this process make this technique particularly attractive for industrial diamond production.

SARBAJIT BANERJEE

Arrays of Binary and Ternary Particles Fabricated by Use of Patterned Microchannels

Patterned arrays of nano- and micron-sized particles have great potential as materials for high-performance electronic and optical devices. In the November 4 issue of *Chemistry of Materials*, researchers Seung-Man Yang and co-workers from the Korea Advanced Institute of Science and Technology report a method for fabricating binary and ternary particle arrays using patterned microchannels. This method began with a poly(dimethylsiloxane) mold containing V-shaped grooves of precise dimensions. These grooves were filled with silica spheres 320 nm or 600 nm in diameter or with polystyrene (PS) spheres 1.01 μm in diameter using a dip-coating technique. The spheres are driven into close-packed arrays in the V-shaped grooves by capillary forces. The confined geometry of the grooves also directs the spheres into a fcc structure with the (100) plane toward the facing surface. After these V-shaped arrays of particles are transferred to a polyurethane film, the resulting new grooves can be filled with spheres of other types and diameters to produce binary particle arrays. For example, 1.01 μm diameter PS spheres could be placed into the grooves between V-shaped arrays of the 320 nm or 600 nm silica spheres. Alternatively, filling those grooves with a mixture of 50 nm diameter silica spheres and 1.01 μm diameter polystyrene spheres leads to a ternary particle array. Subsequent oxygen plasma etching selectively removes the polystyrene particles, leaving patterned, inverted-pore structures in the material. The researchers indicated the potential for using this technique for the fabrication of "display devices, 2D photonic crystals, and ordered open-pores structures" that could be used as "templates for nonspherical aggregates of colloidal particles."

LARKEN E. EULISS

Nanofiber Alumina Enhances Osteoblast Function for Orthopedic Implants

Some key questions in biomaterials address the bonding of bone to implant surfaces for dental and orthopedic applications. In their study on osteoblast function on anisotropic nanoparticulate compounds, researchers from Purdue Univer-

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