Nitrogen-Doped Ultrananocrystalline Diamond Films Exhibit High Room-Temperature *n*-Type Conductivity

Microwave plasma-enhanced chemical vapor deposition has been used by a group of scientists at the Argonne National Laboratory to produce ultrananocrystalline diamond thin films with *n*-type conductivity as high as 143 $\Omega^{-1}cm^{-1}$, much higher than reported for microcrystalline diamond films. The use of typical microcrystalline diamond films doped with nitrogen in electronic devices is precluded by their low room-temperature conductivity. However, nitrogen doping of UNCD films improves the conductivity, as reported by S. Bhattacharyya, O. Auciello, D.M. Gruen, and their co-workers at Argonne in the September 3 issue of *Applied Physics Letters*. The researchers propose that grain-boundary conduction, which increases with increased nitrogen concentration in the growth plasma, is responsible for the observed increase in overall conductivity. While the nitrogen incorporated into the substrate saturates, the grain boundaries continue to change as the nitrogen concentration in the plasma increases.

The ultrananocrystalline diamond (UNCD) films with grain sizes between 2 nm and 5 nm were grown at 800°C on Si(100) and insulating silica using a gas mixture of CH_4(1%)/Ar/N_2(1 to 20%) with a total pressure of 100 torr and 800 W of microwave power. As the fraction of nitrogen in the plasma increased to 5%, the densities of the C_2 and CN radicals increased substantially, as measured by absorption spectroscopy. The density of C_2 radicals increased faster than that of the CN radicals at low nitrogen concentrations. Secondary-ion mass spectroscopy (SIMS) showed a saturation of nitrogen in the diamond films at 2×10^{20} atoms/cm^3 when the nitrogen concentration in the plasma reached 5%. However, the microstructure of the films at these low concentrations did not differ much from the microstructure of undoped films. For films obtained using nitrogen concentrations larger than 10%, the resultant grain size and grain-boundary width increased significantly to 12 nm and 1.5 nm, respectively. High-resolution imaging showed evidence that the grain boundaries were less dense than the grains, which the researchers interpret as evidence of increased sp^2 bonding in the grain boundaries. The conductivity at room temperature increased with nitrogen in the plasma, from 0.016 $\Omega^{-1}cm^{-1}$ (for 1% N_2) to 143 $\Omega^{-1}cm^{-1}$ (for 20% N_2). The highest value reported for nitrogen-doped microcrystalline diamond films in the literature is 10^{-6} $\Omega^{-1}cm^{-1}$.

Results from Hall measurements for 10% and 20% nitrogen in the plasma show that carrier concentration and carrier mobility increased with nitrogen concentration (reaching 1.5×10^{20}/cm^3 and 10 cm^2/Vs for 20% nitrogen in the plasma), exhibiting significantly higher values than other diamond films with *n*-type conductivity. Temperature-dependent conductivity measurements did not produce a linear Arrhenius plot, indicating evidence of multiple conduction mechanisms thermally activated with different activation energies.

The researchers at the Argonne National Laboratory suggest that nitrogen doping within the grains may not be considered the cause of the increase in conductivity in this case, since nitrogen forms a donor level 1.7 eV below the conduction band. Doping of the high-angle grain boundaries in these films is favored by 3–5 eV over doping of the grains based on molecular dynamics simulations. The researchers propose that grain-boundary conduction involving carbon π-states formed at the grain boundaries is responsible for the observed increase in conductivity. Theoretical studies on this mechanism performed at the Argonne National Laboratory have demonstrated that many of these states near the Fermi level are delocalized over several carbon nearest neighbors. Quantitative studies on the electronic transport mechanisms are currently under investigation.

SIARI S. SOSA

Nonlinear Optical Phenomena Observed in Photonic Crystal Fibers

While photonic-crystal fibers (PCFs) have applicability in several fields like telecommunications, nonlinear optics and sensing, amplifiers, and high-power delivery systems, their optical properties are yet to be fully understood. PCFs are made out of an array of microscopic air-holes distributed more or less symmetrically around a solid core of silica, or around a hollow core. An international team of researchers from Los Alamos National Laboratory, the University of Florida, the Universidad Autonoma de Puebla in Mexico, and the University of Bath in the United Kingdom have recently studied optical nonlinear effects in solid-core PCFs by coupling femtosecond pulses at 1.55 μm wavelength to a short-length photonic crystal fiber.

As reported in the August 1 issue of *Optics Letters*, they coupled 170 fs pulses of 1550 nm light from an optical parametric oscillator with an 80-MHz repetition rate (average power 80 mW) into a 95-cm-length solid core (2.5-μm-diameter silica) PFC. The output signal has been spectrally and temporally analyzed, while the fundamental IR pulses were analyzed with a single-shot second harmonic generation frequency-resolved optical-grating (FROG) apparatus. The results of the experiment showed that the output signal depends on the average power of the input signal as follows: For low input signal average powers, only the IR light corresponding to the input wavelengths is detected whereas for input signal above 10 mW, blue-green light is detected in a six-lobed far-field modal pattern. Increasing the power of the input radiation to 22 mW leads to additional yellow light at the output of the fiber with the same far-field spatial characteristics, but slightly rotated. The researchers believe that the visible radiation is the result of a combination of factors: temporal pulse splitting followed by Raman self-frequency shifting and third-harmonic generation.

This study revealed some of the nonlinear characteristics of the PCFs, the temporal and spectral phase dependence of the fundamental pulses furnishing insight in the processes that lead to fre-

Review Articles

The following review articles relevant to materials research have been published recently.

"Quantum Effects in Incipient and Low-Temperature Ferroelectrics (A Review)," by O.E. Kvyatkovskii, *Physics of the Solid State* **43** (8) (2001) p. 1401.

"Collisions of Ions with Surfaces at Chemically Relevant Energies: Instrumentation and Phenomena," by V. Grill, J. Shen, C. Evans, and R. Graham Cooks, *Review of Scientific Instruments* **72** (8) (2001) p. 3149.

"Fluid Flow Phenomena in Materials Processing—The 2000 Freeman Scholar Lecture," by Y. Jaluria, *Journal of Fluids Engineering* **123** (2) (2001) p. 173.

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quency conversion and possibly to supercontinuum generation, increasing the possibility to design nonlinear fibers for dedicated applications and potentially enabling the generation of single-cycle optical pulses in the visible.

IULIA MUNTELE

Magnetostatic Energy May Explain Unusual Ferromagnetic Transition in Erbium

Erbium metal exhibits unusual behavior at the ferromagnetic transition. The first-order transition between ferromagnetic (F) and antiferromagnetic (AF) phases near 19 K demonstrates superheating and supercooling as well as an unusual mechanism behind the phase change. In material with small amounts of impurity, the phase transition is resolved into at least four subtransitions apparently connected with metastable phases occurring within a range of about 2 K. C.S. Durfee and C.P. Flynn at the University of Illinois at Urbana-Champaign account for this phenomenon in terms of magnetostatics which favors transitions through ferrimagnetic intermediaries.

As reported in the July 30 issue of *Physical Review Letters*, some features of the ferromagnetic nucleation in erbium can be explained by conventional methods. However, the researchers determined that the magnetostatic self-energy of the transformed nucleation droplet is enough to supercool the droplet to more than an order of magnitude greater than the observed 1 K. They report that this behavior indicates that nucleation of the erbium phase cannot occur by the normal process of spherical droplets. The researchers instead propose the use of spheroidal droplets of large eccentricity. In spite of the increased surface area (by ~200%) of the spheroidal droplet over that of the spherical droplet, the magnetostatic self-energy is greatly diminished, reducing the barrier to nucleation. These anisotropic shapes represent the preferred path for droplet growth during the nucleation process. The researchers found that for 1 K supercooling, the length of the critical droplet along its major axis is now an order of magnitude larger than expected; however, the magnetostatic energy is still far too big and requires an impossibly large supercooling.

The researchers believe the answer lies in the metastable states accessed during the F-to-AF phase transition and consider ferrimagnetic intermediate (FI) phases, with 2, 4, or 6 spins aligned out of every 8. They believe this explanation offers a low energy route between AF (0 excess spins) and F (all 8 spins aligned) and that magnetostatics again plays a critical part. For the first ferrimagnetic phase the magnetostatic energy is reduced by a factor of 16 with a spheroidal droplet radius that has a surface energy 70% greater than a spherical nucleus. The barrier to nucleation for this FI droplet is now comparable with that of a spherical droplet in which the magnetostatic contribution is neglected. The researchers suggest that this explains the four-stage magnetic transition that has been observed.

JENNIFER BURRIS

Volatile Metal Alkylamides Serve as Precursors for Vapor Deposition of High-Dielectric-Constant Gate Insulator Materials

The speed and capacity of computers have been doubling every year or two, following Moore's law. These improvements in the power of microelectronics have been achieved largely by shrinking their dimensions. The smallest components in circuits are gate insulators,

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