

### **One-Dimensional Heterostructures Fabricated in InAs/InP Nanowhiskers**

Previously, researchers have grown one-dimensional semiconductor nanowhiskers and then made diodes and bipolar transistors *between* crossed, differently doped whiskers. However, researchers from the Solid-State Physics/Nanometer Consortium at Sweden's Lund University have fabricated a heterostructure device *within* a single 40-nm-diameter InAs whisker. They used size-selected Au aerosol seed particles along with chemical-beam epitaxy (CBE) to sprout their nanowhiskers from GaAs substrates. These tiny InAs pillars contain either one or a sequence of InP barriers, ranging from 1.5 nm to 100 nm thick, and boast atomically sharp interfaces between the layers.

After depositing the Au seed particles into (111)B GaAs substrates, M.T. Björk and colleagues used CBE to grow the long whiskers at 420°C. The beam pressures were 0.3 mbar for the trimethyl indium (TMIn) source, 2.0 mbar for the tertiary butyl arsine source, and 3.0 mbar for the tertiary butyl phosphine source. The alternating InAs and InP layers were then grown by switching between the two Group V sources while the TMIn source was extinguished. As reported in the February 4 issue of *Applied Physics Letters*, the researchers found that the thicknesses were highly reproducible, and transmission electron microscopy (TEM) images showed that growth can occur in the (001) direction as well as in the more commonly reported (111)B direction.

The low growth rate (about 1 monolayer per second) and high vapor pressures of the Group V sources is responsible for the monolayer abruptness of the interfaces as imaged by high-resolution TEM, according to the researchers.

The researchers report that measurements of thermionic emission across an InP heterobarrier are most telling. They demonstrated that the thermally excited currents follow the expected Arrhenius relation and deduced an InP barrier height (0.6 eV) that is very close to the bulk value. This result is gratifying, said the researchers, as it shows that the whiskers' tiny cross sections permit efficient lateral relaxation of the two materials. This allows a combination of materials with dissimilar lattice constants that is not possible with ordinary epitaxy on a larger scale, due to, for example, the incorporation of misfit dislocations once the critical thickness of several monolayers is exceeded.

The researchers also proposed new branches of physics phenomena and new families of device structures that can be

realized with these semiconductor nanowhiskers.

"These results open the possibility of realizing novel 1-D systems, such as heterostructures integrated in scanning probe or field-emission tips, 1D-0D-1D resonant tunneling devices, and one-dimensional superlattice arrays of intercoupled quantum dots," said Björk, "and devices for quantum optics and photonics applications."

RICHARD N. LOUIE

### **Intermittency of CdSe Quantum-Dot Photon Emissions Follows a Power Law Distribution**

The development of sources that emit single photons separated in time is essential to the success of quantum optics applications such as quantum cryptography. This time-separated emission phenomenon is called "antibunching," since none of the emissions occurs simultaneously; emission of two or more photons simultaneously is called "bunching." Antibunching has been achieved over short time intervals through fluorescence of atoms, molecules, quantum dots (QDs), and single nitrogen vacancy centers in crystals as well as electroluminescence from QDs in *p-i-n* junctions. But over longer time periods, these same systems tend to turn on and off at irregular intervals, a phenomenon known as "intermittency." By studying the emission behavior of CdSe quantum dots over an unprecedented time scale (from nanoseconds to tens of seconds), researchers at the Ecole Normale Supérieure et Université Pierre et Marie Curie in Paris have found that intermittency follows a power law, instead of the normal exponential decay seen in two-state systems with constant on/off rates.

As reported in the December 1, 2001, issue of *Optics Letters*, CdSe quantum dots of 1.8-nm radius were deposited on a glass coverslip by spin coating a nanomolar solution of QDs in butanol and a thin film of poly methyl (methacrylate). These QDs were then excited by the 514-nm line of an Ar<sup>+</sup> laser, and the fluorescence photons were detected by a 50/50 nonpolarizing beam splitter followed by two (start and stop) single-photon avalanche photodiodes. A picosecond time analyzer was used to measure delays between emission times of the photons. A histogram of coincidence counts versus photon time delay shows the characteristic dip at zero time delay that is the signature of antibunching systems. There is a separation between all photon emissions; no emissions are occurring at the same time (time delay = 0).

The researchers used the normalized autocorrelation function (ACF) to analyze

the emission properties over time scales ranging from 100 ns up to 1000 s. From 100 ns up to 100  $\mu$ s, the ACF is nearly constant, indicating no intermittency—complete antibunching is observed. After 100  $\mu$ s, the ACF slowly decreases before dropping off abruptly as the time approaches the measurement duration. Increasingly longer on and off states occur as the measurement duration increases. This behavior cannot be explained by exponential decay equations used to describe two-state (on and off) systems. Rather, a power law dependence is necessary to model the densities of probability of on and off states.

The researchers caution that because of this power-law dependence, QDs cannot be considered stationary systems at long time scales, so conventional ACF analysis should be used with care.

TIM PALUCKA

### **3D Nanoarray Microporous Carbon Structure Achieves High Surface Area**

Microporous carbon has become of great interest in recent years due to its ability to store natural gas and act as the electrodes of an electric double-layer capacitor. As reported in the December 17, 2001 issue of *Chemistry of Materials*, researchers from Tohoku University were able to synthesize a three-dimensional (3D) nano-array microporous carbon structure, achieving a [Brunner-Emmet-Teller (BET) method] surface area as high as 3600 m<sup>2</sup>/g, using zeolite Y as the template.

The researchers used a three-step method to fill carbon into the nanochannels of zeolite Y. They heated the zeolite/poly(furfuryl alcohol) (PFA) composite to 700°C in N<sub>2</sub> and then used chemical vapor deposition of propylene to introduce carbon. They then heat-treated the composite at 900°C under N<sub>2</sub> flow.

The x-ray diffraction pattern revealed that carbons liberated from the zeolite framework showed intense peaks with highly ordered parts and periodicity of about 1.4 nm, corresponding to the spacing of the {111} plane of zeolite Y. High-resolution transmission electron microscopy (HRTEM) showed the microporous carbon with excellent 3D ordering and periodicity of about 1.3 nm. HRTEM also showed no signs of stacking structure of graphene sheets or any single layers inside carbon-carbon particles.

Another noticeable characteristic of the synthesized carbon was its high surface area from N<sub>2</sub> adsorption, said the researchers. They were able to achieve a high surface area without the usual chemical activation using KOH, reducing the presence of mesoporosity and the size of pore

distribution. These characteristics of carbon led to better filling of carbon into the zeolite nanochannels, which are shown by nuclear magnetic resonance analysis.

Since the highly ordered structure suggested the absence of mesoporosity, the researchers concluded that one possible carbon structure may be "a curved graphene structure...accommodated to the curved inner surface of the zeolite nanochannels."

KINSON C. KAM

### Theories of Polymer Crystallization Challenged by Molecular Simulations

A team of researchers at the University of Massachusetts has demonstrated their modeling results on polymer crystallization from solution in which entropic barriers control the initial lamellar thickness by initiation of crystal nuclei. The nuclei then grow by chain absorption at the crystalline interface, and the lamellae thicken in a cooperative process requiring mobility of all chains in the crystal. These results challenge the conventional Lauritzen-Hoffman (LH) theory and its generalizations.

In contrast to the crystallization of small molecules, the crystallization of polymers from solution is still poorly understood. Polymer molecules can participate in different initial nuclei, which leads to entropic frustration and incomplete crystallization, in which the polymer chains fold back and forth to form crystalline lamellae. So far, thermodynamics estimates have failed to predict the initial lamellar thickness, and all estimates are about 2 orders of magnitude higher than the 10 nm observed. There is also some controversy about the growth mechanism of the lamellae. As reported in the November 19, 2001, issue of *Physical Review Letters*, the group used Langevin dynamics simulations to reinvestigate these problems.

The results of the dynamics simulations show that the initial crystallization from solution does not occur by spinodal dynamics, but through a nucleation and growth mechanism, in which the initial lamellar thickness is dictated by free-energy barriers. The initial thickness is spontaneously selected, and the chains thicken by negotiating free-energy barriers before asymptotically approaching a thickness that is much smaller than the thermodynamically predicted extended chain limit. Chain growth occurs by simultaneous adsorption and crystallographic registry of diffusing chains at the growth front. In contrast to the LH model, this step is not hindered by an energy barrier. The chains then rearrange to form stems that are commensurate with the

crystal thickness at the growth front.

M. Muthukumar, Barrett Professor in the Department of Polymer Science and Engineering, said, "Our results suggest that the definitions of quench depth and equilibrium melting temperature, which depend on the equilibrium lamellar thickness, need to be redefined. This opens up 40 years of accumulated data for re-analysis."

CORA LIND

### Hypersensitization Improves Performance of Rare-Earth-Doped Active Waveguides

The photosensitivity of optical waveguides has been enhanced in the past with the addition of hydrogen. The price for such sensitivity-enhancement includes thermal instability, additional absorption due to hydrogen-induced bands, lower gain, and out-diffusion issues during device fabrication. J. Canning and K. Sommer of the Optical Fibre Technology Centre at the University of Sydney have resolved these issues by using hydrogen hypersensitization in active optical waveguides.

Typically, waveguides are patterned by UV irradiation. To effectively demonstrate the advantages of hypersensitized fibers as compared with untreated and hydrogen-loaded fibers, a total of six specimens were measured for small signal gain and lifetime according to the following plan, as reported in the December 1, 2001, issue of *Optics Letters*. Two different types of fibers were used in the experiments. The first batch, consisting of three samples, was 12% germanosilicate fibers doped with 0.1 mol%  $\text{Er}^{3+}$ . The second batch, consisting also of three samples, was 17% phosphosilicate fibers doped with 0.3 mol% and 3 mol% of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ , respectively. In addition, three pre-irradiation treatments were applied to the samples. Two samples, one from each batch, were not modified. Two samples—again, one from each batch—were fully loaded with hydrogen at 200 atm, 80°C, for four days. The remaining two samples were hypersensitized samples; that is, hydrogen was introduced and the samples were given a preliminary exposure before the hydrogen was allowed to out-diffuse. Gratings in the fibers were subsequently written with a 244-nm (germanosilicate fibers) and a 193-nm (phosphosilicate) UV laser. The small-signal gain coefficient was measured using a tunable laser and a 980-nm pump. A chopper and an oscilloscope were used to measure the excited-state lifetime.

In the germanosilicate samples, small signal gain was reduced with the intro-

duction of hydrogen throughout the 1520–1560-nm range, according to the researchers. They reported that the hypersensitized sample fared better than the fully loaded samples. Hydrogen caused little deviation in the upper excited-state lifetime, they said.

Small signal gain in the hypersensitized phosphosilicate fiber was comparable to that of the unmodified fiber. Lifetime in the hypersensitized fiber was slightly lower than that of the untreated fiber. The fully loaded fiber suffered significantly in both signal attenuation and excited-state lifetime.

The researchers concluded from this set of experiments that hypersensitization is a readily available method for improving stability, reliability, and efficiency of optical fibers and waveguides.

JUNE LAU

### Molecules Designed to Mimic Bone at the Nanolevel

A research team at Northwestern University led by Samuel I. Stupp, the Board of Trustees Professor of Materials Science, Chemistry, and Medicine, has designed molecules that self-assemble into a three-dimensional structure that mimics the key features of human bone at the nanoscale level. These features include collagen nanofibers that promote mineralization and mineral nanocrystals. Collagen is found in most human tissues, including the heart, the eye, blood vessels, skin, cartilage, and bone, and gives these tissues their structural strength.

As reported in the November 23, 2001, issue of *Science*, the researchers created self-assembled nanofibers (~8 nm in diameter) that resemble the collagen fibrils of real bone in shape and size. When the nanofibers were exposed to solutions containing calcium and phosphate ions, the fibers became covered with hydroxyapatite crystals. These thin, rectangular mineral wafers grew on the nanofibers in a direction parallel to the fiber's length, mimicking hydroxyapatite-crystal growth on collagen in the formation of real bone.

According to the researchers, the assembly of the nanofibers themselves can be reversed by changing the pH level of the fibers' environment. The fibers also can be polymerized or cross-linked by oxidation to give them additional strength, a process that also can be reversed. The researchers said that the versatility of the nanofiber system offers the possibility of using the organic fibers as "cargo carriers," possibly for drug delivery to a specific point in the body. Natural enzymes found in the body can disassemble the fibers so that their cargo can be released.