

Preferential Growth of Metallic SWNTs Achieved

One obstacle to the implementation of single-walled carbon nanotubes (SWNTs) in electronic devices is that their synthesis results in a mixture of conducting and semiconducting species. Progress has been made in separating SWNTs based on their conductivities, which is determined by chirality. Some progress has been made in controlling SWNT structure during growth (e.g., semiconducting SWNTs are produced preferentially by plasma-enhanced chemical vapor deposition), demonstrating that somewhat different mechanisms lead to different chiralities. Recently, A.R. Harutyunyan and co-researchers at the Honda Research Institute, Columbus, Ohio, in collaboration with T.M. Paronyan of the University of Louisville, S.M. Kim of Purdue University, and their colleagues, were able to increase the fraction of CNTs with metallic conductivity grown from Fe nanocatalysts from 33% to a maximum of 91% by varying the conditions under which the catalyst was annealed.

As reported in the October 2 issue of *Science* (DOI: 10.1126/science.1177599;

p. 116), Harutyunyan and co-researchers annealed *in situ* Fe nanocatalysts deposited onto a flat SiO₂/Si support, using an ambient atmosphere of He or Ar, and varying ratios of H₂ and H₂O. Using methane as the carbon source, SWNT synthesis was performed at 860°C. The researchers observed with scanning electron microscopy that increasing the concentration of reductive species (Ar:H₂ was increased from 9:1 to 8:2 at 840 Torr with ~3.5 mTorr H₂O) during catalyst conditioning resulted in higher densities of SWNTs on the substrate. This led them to perform a systematic study of SWNT growth on catalysts annealed *in situ* under varying ambient conditions. The ratio of metallic to semiconducting tubes was obtained by measuring the SWNT's Raman breathing modes, specifically, $R = I_{\text{met}}/I_{\text{sem}}$ where I_{met} and I_{sem} are the integrated intensities of the metallic and semiconducting SWNTs, respectively. The researchers observed an increase in R by (1) replacing Ar with He; (2) increasing the H₂ content in the Ar-H₂ atmosphere; and (3) increasing the annealing time from 1 minute to 10 minutes. A very high R value of 20.2, which corresponds to over 90% metallic SWNTs, was

obtained with a He:H₂ ratio of 8:2 and an annealing duration of 10 minutes.

The researchers verified their Raman spectra analysis by measuring field-effect transistor performance for 47 individual SWNTs and characterizing them according to their source-drain current. Another set of experiments demonstrated that the catalyst annealed in the presence of H₂O in the ambient atmosphere together with He promotes the growth of metallic tubes whereas semiconducting tubes are favored by catalysts annealed with an ambient atmosphere of H₂O and Ar. The researchers also investigated the mechanism of tube formation with *in situ* transmission electron microscopy of the Fe nanocatalysts under varying gaseous environments in analogy with the SWNT-synthesis conditions. Differences in both morphology and coarsening behavior of the nanocatalyst were observed.

The researchers said that "these catalyst rearrangements demonstrate that there are correlations between catalyst morphology and resulting nanotube electronic structure and indicate that chiral-selective growth may be possible."

STEVEN TROHALAKI

Quasicrystalline Order Revealed in Nanoparticle Superlattices

Quasicrystals are a class of materials that show sharp diffraction peaks despite presenting forbidden symmetry operations in classical crystallography. D.V. Talapin and M.I. Bodnarchuk from the University of Chicago; E.V. Shevchenko from Argonne National Laboratory; and X. Ye, J. Chen, and C.B. Murray from the University of Pennsylvania, have reported in the October 15 issue of *Nature* (DOI: 10.1038/nature08439; p. 964) that different binary nanoparticle colloidal systems can self-assemble into 12-fold rotational quasicrystalline order. According to the researchers, the compositional flexibility demonstrated that quasicrystal ordering could be a relatively common phenomenon in nanocrystal solids, with suitable size ratios between particles.

sharing a common vertex. In proximity to the (3².4.3.4) phase in the binary phase diagram of these nanoparticles, the researchers observed reproducible formation of a type of binary superstructure without translational symmetry. They observed that these structures showed sharp electron diffraction patterns revealing dodecagonal rotational symmetry, a symmetry operation forbidden in periodic structures. The researchers identified these self-assembled nanoparticle superstructures as dodecagonal quasicrystals (DDQC), a phase that formed also from colloidal solutions containing 12.6-nm Fe₃O₄ and 4.7-nm Au nanocrystals, and 9-nm PbS and 3-nm Pd nanocrystals, with size ratios between particles of ~0.43.

The researchers said that the space-filling factor had a significant effect on the relative stabilities of binary nanoparticle phases, and the quasi-periodicity could be a result of maximizing the entropy of arrangement of square and triangular "tiles." They consider that the discontinuity in the entropy density corresponding to the DDQC state might provide a mechanism for locking the quasicrystalline state over a range of nanocrystal concentration ratios. The researchers think that these studies will provide insight into the formation of the quasicrystal phase in atomic systems, and can be used as a convenient platform for detailed investigation of quasicrystal properties.

JOAN J. CARVAJAL

Addendum

David N. Seidman and Krystyna Stiller, Guest Editors of the theme "A Renaissance in Atom-Probe Tomography" (*MRS Bulletin*, October 2009), note that in 1973, J.A. Panitz invented the 10-cm atom probe (discussed on p. 745)—now called the imaging atom probe—which is the progenitor of all atom-probe tomographs, citing the following references: J.A. Panitz, *Rev. Sci. Instrum.* **44**, 1034 (1973) and J.A. Panitz, "Field Desorption Spectrometer," U.S. Patent 3868507 (1975).

The researchers obtained the quasicrystalline nanoparticle assemblies by evaporating relatively concentrated colloidal solutions of 13.4-nm Fe₂O₃ and 5.0-nm Au monodisperse nanoparticles capped with oleic acid and dodecanethiol molecules, respectively, in tetrachloroethylene at 50°C under reduced pressure (~3.2 kPa) on a carbon-coated transmission electron microscopy grid or a silicon nitride membrane tilted by 60° or 70°. The researchers used the surfactant molecules to introduce short-range steric repulsion that counterbalanced the van der Waals forces and prevented uncontrollable aggregation of nanocrystals in the colloidal solution. They observed that during this process the nanocrystals self-assembled in AlB₂- and CaB₆-type phases, and on the (3².4.3.4) Archimedean tiling structure, depending on the Fe₂O₃-to-Au nanoparticle ratio. This structure is formed by five planar polygons (three triangles and two squares) sharing a common vertex in such a way that they fill the plane with no overlaps and no gaps, depending on the Fe. The nomenclature of these structures lists in order the polygons that meet at each vertex using integers that correspond to the numbers of sides of the polygons. So, the (3².4.3.4) structure consists of two triangles sharing a common edge, surrounded by two squares at each side of the triangles, and filling the empty space by another triangle, all of them

Polymer Photodetector Developed with High Detectivity Across Broad Spectral Range

Photodetectors sensitive to the full UV-visible to near-infrared spectrum are very desirable for scientific and technological applications, but conventional semiconductor detectors are limited to narrower subbands of the spectrum. Full coverage thus requires separate sensors for different subbands, which is a complicated and costly solution at best. As published in the September 25 issue of *Science* (DOI: 10.1126/science.1176706; p. 1665), a group of researchers have addressed this problem with a new polymer photodetector (PPD) with broad spectral response and unusually high detectivity. X. Gong and A.J. Heeger from the University of California in Santa Barbara and CBrite Inc., Y. Cao from South China University of Technology, and their colleagues have built a PPD that delivers a response from 300 nm to 1450 nm in a device that incorporates a small bandgap conjugated polymer with a fullerene-derivative in the active region.

Gong and co-workers fabricated their

PPD by spin-casting a mixture of poly(5,7-bis(4-decanyl-2-thienyl)-thieno (3,4-*b*) diathiazole-thiophene-2,5) (PDDTT) and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) between an InSnO₃ (ITO) anode and Al cathode. The PDDTT:PC₆₀BM forms an interpenetrating donor and acceptor bulk heterojunction network in the active layer, allowing efficient photo-generation and collection of carriers. The researchers said that shot noise from dark current limits detectivity and, under this assumption, attempt to maximize detectivity by incorporating additional materials in a multilayer geometry to block or suppress dark current. They fabricated a number of devices including layers of various polymers and fullerene-derivatives, and measured the photocurrent and dark current of each device at -100 mV bias. From these data they calculated the detectivity and found the best response from devices with layers of polystyrene-N, N-diphenyl-N,N-bis(4-n-butylphenyl)-(1,10-biphenyl)-4,4-diamine-perfluorocyclobutane (PS-TPB-PFCB) and C₆₀. The layering order of this device was ITO/PEDOT/PS-TPD-PFCB/PDDTT:

PC₆₀BM/C₆₀/Al. The C₆₀ layer prevents photogenerated holes from reaching the Al cathode and the PS-TPD-PFCB blocks electrons from the ITO anode, resulting in a dramatically decreased dark current. PEDOT is poly(3,4-ethylene-dioxy-thiophene).

For incident wavelengths of 300 nm to 1450 nm the calculated detectivity of this device is near or above that of Si and InGaAs detectors, ranging from 10¹⁴ Jones to 10¹² Jones (where Jones = cm Hz^{1/2}/W). A further advantage of the PPD over InGaAs is that this impressive detectivity is achieved at room temperature, whereas InGaAs photodetectors must be cooled to near 4.2 K to achieve this detectivity. The researchers also demonstrated that the PPD has a linear dynamic range much larger than InGaAs photodetectors and almost as large as Si photodetectors. Given the favorable comparison to conventional photodetectors and the simple, inexpensive fabrication technique, Gong and co-workers are optimistic that their polymer photodetector will prove valuable to a variety of applications.

ALISON HATT

Pinning Down Superconductivity to a Single Layer

Using precision techniques for making superconducting thin films layer-by-layer, G. Logvenov, A. Gozar, and I. Božović of Brookhaven National Laboratory have identified a single layer responsible for one such material's ability to become superconducting. The technique, described in the October 30 issue of *Science* (DOI: 10.1126/science.1178863; p. 699), could be used to engineer ultrathin films with "tunable" superconductivity for higher efficiency electronic devices.

"We wanted to answer a fundamental question about such films," said physicist and group leader Ivan Božović. "Namely: How thin can the film be and still retain high-temperature superconductivity?"

The thinner the material (and the higher its transition temperature to a superconductor), the greater its potential for applications where the superconductivity can be controlled by an external electric field. "This type of control is difficult to achieve with thicker films, because an electric field does not penetrate into metals more than a nanometer or so," Božović said.

To explore the limits of thinness, Božović's group synthesized a series of films based on the high-temperature superconducting cuprates (copper-oxides)—materials that carry current with no energy loss when cooled below a certain transition temperature. Since zinc is known to suppress the superconductivity in these materials, the scientists systematically substituted a small amount of zinc into each of the copper-oxide layers. Any layer where the zinc's presence had a suppressing effect would be clearly identified as essential to superconductivity in the film.

"Our measurements showed that the zinc doping had essentially no effect, except when placed in a single, well-defined layer. When the zinc was in that layer, the superconductivity was dramatically suppressed," Božović said.

The material studied by Božović's team was unusual in that it consists of layers of two materials, one metallic and one insulat-

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ing, that are not superconductors on their own, but rather exhibit superconductivity at the interface between them. The layer identified as essential to the superconductivity by the zinc-substitution experiment represents the second copper-oxide layer away from the interface.

The scientists found that the presence of zinc had no effect on the transition temperature at which superconductivity sets in, ~32 K (-241°C), except when placed in that particular layer. In the latter case, the scientists observed a dramatic drop in the transition temperature to 18 K (-255°C). The reduction in transition temperature provides a clear indication that that particular layer is the “hot” one responsible for the relatively high temperature at which superconductivity normally sets in for this material, according to the researchers.

“We now have a clean experimental

proof that high-temperature superconductivity can exist, undiminished, in a single copper-oxide layer,” Božović said. “This piece of information gives important input to our theoretical understanding of this phenomenon.”

Božović said that, in the material he studied, the electrons required for superconductivity actually come from the metallic material below the interface. They leak into the insulating material above the interface and achieve the critical level in that second copper-oxide layer.

But in principle, he said, there are other ways to achieve the same concentration of electrons in that single layer, for example, by doping achieved by applying electric fields. That would result in high-temperature superconductivity in a single copper-oxide layer measuring just 0.66 nm.

From a practical viewpoint, this discovery opens a path toward the fabrication of

electronic devices with modulated, or tunable, superconducting properties which can be controlled by electric or magnetic fields, said the researchers.

“Electronic devices already consume a large fraction of our electricity usage—and this is growing fast,” Bozovic said. “Clearly, we will need less-power hungry electronics in the future.”

Superconductors, which operate without energy loss—particularly those that operate at warmer, more-practical temperatures—may be one way to go.

According to the researchers, their layer-by-layer synthesis method and ability to strategically alter individual layers’ composition might also be used to explore and possibly control other electronic phenomena and properties that emerge at the interfaces between layered materials.

Hierarchical Topographies Created by Controlled Evaporation of a Block Copolymer Solution

Hierarchically ordered materials tend to have unique physical properties. For instance, the lotus leaf has both micro- and nanostructures which contribute to its superhydrophobicity. To produce materials with useful properties such as superhydrophobicity, simple methods for making hierarchical materials must be established. Block copolymers provide a way of creating nano-patterned surfaces because of their ability to self-assemble into their constituent blocks. Zhiqun Lin, Suck Won Hong, and Jun Wang at Iowa State University have shown that controlled evaporation of a diblock copolymer solution creates a serpentine-like microstructure, which can further be processed to have nanostructures.

As described in the October 19 issue of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.200903552; p. 8356), Lin and co-workers prepared a solution of polystyrene-*block*-poly(methylmetha-

crylate) (PS-*b*-PMMA) in toluene at a concentration of 0.13 mg/mL. The molecular weight of each block was 45.9 kg/mol and 138 kg/mol for PS and PMMA, respectively. This solution was held between a fused silica lens (1 cm diameter) and a silicon wafer by capillary forces. As the solution evaporated toward the center of the lens, concentric rings of the block copolymer were deposited on the silicon wafer surface. These rings had an undulating or “serpentine” morphology on the micron scale. The spacing between the characteristic features was approximately 20 μm and the height was approximately 100 nm. To further change the morphology, the researchers aged the films by exposing them to acetone vapor for up to 12 hours. After exposing the films to acetone vapor, the microtopography changed from “serpentine-like” to “mesh-like”—with distinct holes forming the “mesh-like” structure. At the nanoscale, atomic force microscopy and transmission electron microscopy imaging showed that the acetone vapor caused the polystyrene blocks to phase-

segregate into hexagonally packed, cylindrical nanodomains ~39 nm in diameter. The surface chemistry was analyzed by x-ray photoelectron spectroscopy (XPS) and showed that aging the films with acetone vapor increases the carbonyl (O=C=O) signal at 289.1 eV relative to the hydrocarbon (C-C or C-H) signal at 285.0 eV.

The researchers attributed the “serpentine-like” microstructure to fingering instabilities which arise during progressive “stick-slip” motion of the three phase contact line as the solvent evaporates. The researchers propose that polystyrene initially forms at the top of the film due to its lower surface tension. XPS results demonstrated that the PMMA matrix reorients toward the surface after exposure to acetone vapor. This caused the polystyrene to form cylindrical nanodomains oriented perpendicular to the surface. Lin and colleagues propose that controlled self-assembly methods such as these allow for simple fabrication of hierarchical structures without using lithography.

SCOTT COOPER

How to Choose In-plane Ferroelectric Polarization States in Rhombohedral BiFeO₃

An international team of researchers have devised a way to reliably manipulate the ferroelastic polarization states of rhombohedral multiferroic materials that allows coupling to the strain and magnetic properties of these materials.

“The control of polarization switching to create different domain patterns with

predefined in-plane domain orientations is key to applications which are based on the physical properties of domain walls or on the coupling of ferroic order parameters,” said N. Balke of Oak Ridge National Laboratory in explaining the potential impact of their discovery.

As reported in the October 11 on-line issue of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2009.293), the researchers used the electric field from a moving

piezoresponse force microscope (PFM) tip to deterministically generate domain states in BiFeO₃ (BFO), including long-sought closure domains. Closure domains are ferroic domains of position and orientation such that flux lines from larger, adjacent domains close upon themselves (see, e.g. www.answers.com/topic/closure-domain). The tip motion that broke the rotational symmetry of the electric field was a crucial element that allowed the

researchers to achieve this advancement compared to previous studies.

Few materials allow the manipulation of the strain and magnetic states of a multiferroic through direct application of an electric field, because the stable polarization states in most materials are antiparallel and couple similarly to the other order parameters. This is not so for rhombohedral structures, which can switch to one of four energetically equivalent up- or down-polarized states. M. Huijben, Y.H. Chu, and R. Ramesh of the University of California, Berkeley synthesized samples of rhombohedral (100) BFO to take advan-

tage of this. The BFO was deposited atop leads composed of SrRuO₃ (SRO) all on a TiO₂-terminated (001) SrTiO₃ (STO) substrate to promote growth of BFO.

The phase field modeling of S. Choudhury and L.Q. Chen of Pennsylvania State University showed that all four polarization states of BFO can be accessed by the same switching field due to rotationally invariant symmetries in the material and the electric field using phase-field simulations. How then to manipulate the ferroelectric domains?

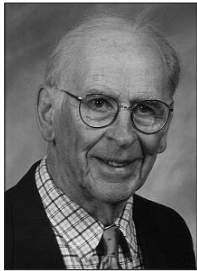
Balke and her co-workers at Oak Ridge, S. Jesse, A.P. Baddorf, and S.V. Kalinin,

found that they could break the symmetry by applying a voltage to a moving PFM tip. They showed that they could repetitively produce domain patterns this way, including a line of closure domains.

"This work shows that it is possible to control the switching process to utilize all new possible functionalities," said Balke, "whether these are local strain sensors, multi-level resistance devices, or information storage devices that write electrically and read magnetically."

JIM RANTSCHLER

News of MRS Members/Materials Researchers



W. Conyers Herring

William Conyers Herring passed away at his home in Palo Alto, California, on July 23, 2009 at the age of 94. For over five decades he made insightful contributions in both materials science and solid-state physics—a unique example of

the value of interdisciplinary research. His theories of capillary phenomena, diffusion-limited plasticity in metals, mechanical behavior of small particles, sintering, and thermionic behavior were recognized in 1980 when he received the Materials Research Society Von Hippel Award with the citation, "Demonstration that whiskers of high crystalline perfection would exhibit extraordinary mechanical properties. He is also held in esteem for his theoretical contributions to the understanding of surfaces and surface tension."

In the same year he received the James Murray Luck Award for Excellence in Scientific Reviewing by the National Academy of Sciences in recognition of his scholarly, comprehensive reviews of thermionic, magnetic, and transport phenomena that are widely cited today.

Earlier in 1959 he was awarded the Oliver E. Buckley Award of the American Physical Society for his major contributions to electronic band theory and its applications.

When Conyers started school at five years old in the small town of Parsons, Kansas he had already taught himself how to read so well that he was placed in the fifth grade. His father's death when he was 13 left the family impoverished, but the following year he was able to enroll in the University of Kansas with a four-year scholarship. He graduated with a major in

astronomy and then switched his focus to solid-state physics when he went to Princeton University, where he particularly enjoyed being able to study independently with few required courses. There, a small group including Eugene Wigner and his graduate students John Bardeen, Frederick Seitz, and Conyers created the modern band theory of solids. Conyers received his degree in 1937 and spent the following two years as a National Research Council fellow at the Massachusetts Institute of Technology. There he introduced the orthogonalized plane wave (OPW) method, the first workable scheme for calculating electronic energy bands in solids, and with A.G. Hill used it to calculate the band structure of beryllium.

Conyers served in the Division of War Research at Columbia University during the second World War. In 1946, after a short time in the Applied Mathematics Department at the University of Texas, he took a position as a member of the technical staff at the Bell Telephone Laboratories, Murray Hill, New Jersey. In that same year he married Louise Preusch who had just graduated from Barnard in math and physics. They made their home in nearby Summit, where their four children Lois, Alan, Brian, and Gordon were born and raised.

Conyers created the theoretical physics department from the strong group already existing at Bell that soon was recognized to be preeminent and a mecca for visitors coming from around the world. Conyers and Louise were gracious hosts and made many friends. He kept himself and others well informed of the rapid advances being made by reading the latest journals as soon as they arrived at the extensive Bell library. He organized references he considered significant by subjects on three-by-five cards containing multi-references with terse comments all

written in long hand. In order to keep current with advances in Russia during the cold war (not wanting to wait for problematic translations) Conyers simply learned to read Russian. He regularly carried his card file in a famous black suitcase, willingly serving the community as a one-man Google—actually a more useful one, because he had already filtered out the extraneous. He was not only known as a fountain of knowledge, but also for his helpful way of sharing, treating everybody with respect and quietly providing his own keen insights. Wigner once remarked [to me] that whenever there was something he wanted to know (in solid state) the first thing he did was to go to Conyers. His review of exchange among itinerant electrons that started as a chapter and turned into a book on magnetism was one of the first recognitions of the role of collective excitations in metals. John H. Van Vleck in reviewing the book (*Physics Today*, April 1967) said that "the preprint at Harvard was so bulky it was usually called the telephone book because of its origin at Murray Hill and its accuracy, attention to detail and usefulness, but it has one detail that the telephone book lacks—the quality of being critical in the best sense of the word."

Conyers moved to Stanford University as Professor of Applied Physics in 1978. He and Louise became active members in the campus community, and he continued productive research activities. Conyers had many outside interests. He was an avid tennis player and a wit who could produce a clever limerick spontaneously. He was a devout Christian who believed that theology underlies science because "science is ultimately based on leaps of intuition and aesthetic perceptions." Those who knew him cherish memories of this remarkable man.

THEODORE H. GEBALLE