

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