Conjugated Polymer Film Fluorescence Enhances Images of Latent Fingerprints

Latent fingerprints—those left on surfaces without any ink—are often a critical clue for investigators at crime scenes. However, the high-sensitivity methods currently used in forensic science to detect latent fingerprints are cumbersome and difficult to employ. Now, in a recent issue of *Chemical Communications* (Issue 16, DOI: 10.1039/b902316j, p. 2112), G. Kwak, W.-E. Lee, W.-H. Kim, and H. Lee of Kyungpook University in Korea introduce a method of using a conjugated polymer thin film and florescent imaging for rapid, reusable latent fingerprint detection that may help overcome these issues.

The highly fluorescent conjugated polymer poly[1-phenyl-2-(p-trimethylsilyl) phenylacetylene] (PTMSDPA) is known to have a large (0.26) fractional free volume as a film, which allows chemicals to easily diffuse into it. The research group previously determined that the intensity of fluorescence of PTMSDPA significantly increases when it absorbs certain chemicals, and speculated that this might also be the case for materials on human skin. To test this hypothesis, the group first exposed a free-standing, 30-μm-thick film of PTMSDPA to a sample of simulated human sebum (a 50:50 wt% mixture of a lipid standard and a fatty acid standard) and found that the fluorescent intensity of the film under UV illumination increased by more than an order of magnitude shortly after contact with the simulated sebum. Notably, no lateral diffusion of the fluorescence increase was observed until 30 minutes after the first exposure, suggesting that any spatial patterns (i.e., fingerprints) would persist in the fluorescence.

The group next directly deposited a real fingerprint on a similar film of PTMSDPA, and obtained images of the polymer's fluorescence under UV illumination. The images show the fingerprint pattern with high resolution, to the point that pores on the ridges are more evident than in conventional chemical imaging techniques. The group was further able to successfully transfer latent fingerprints to the PTMSDPA film from glass, steel, and polyethylene terephthalate (PET) plastic by gently pressing the film onto these surfaces. Transfers from paper were not successful, which the researchers suggest is because of the paper's porosity and roughness. The group was able to erase a fingerprint image on the film by washing it with acetone, and demonstrated the re-use of a film to detect a second print.

These results demonstrate that polymer thin films and UV fluorescent imaging may be the key to simple, rapid, and reusable latent fingerprint detection, which would earn the thanks of crime scene investigators everywhere.

Colin McCormick

Percolation Model Developed to Describe Charge Transport in FETs Constructed from CNT Networks

Films composed of random carbon nanotube (CNT) networks are increasingly being used for electronic applications. The low cost and flexibility of submonolayer CNT films have led to their use as sensors and as field effect transistors (FETs). Individual CNTs have been reported to have field effect mobilities of 10,000–100,000 cm^2/Vs. However, carbon nanotube network FETs (CNTN-FETs), which contain both metallic and semiconducting CNTs, display mobilities on the order of 10 cm^2/Vs for unprocessed films and 80 cm^2/Vs after the films are processed to break metallic network conduction. Because only the semiconducting CNTs can have their conductance modulated, it is critical to have semiconducting CNTs percolate the film, whereas a percolative metallic network would short out the device. Controlling tube density, tube-tube junction characteristics, and the fraction of tubes that are semiconducting may all lead to improved device performance. Recently, M.A. Topinka, M.W. Rowell, D. Goldhaber-Gordon, and M.D. McGehee of Stanford University and the SLAC National Accelerator Laboratory, Menlo Park, and D.S. Hecht and G. Gruner of the University of California, Los Angeles have investigated how current flows through CNTN-FETs, and have provided evidence for three possible types of CNTN-FETs with fundamentally different gating mechanisms. They have also developed an electronic phase diagram for CNTN-FETs.

As reported in *Nano Letters* (DOI: 10.1021/nl803849e; Web publication: March 30), Topinka, Goldhaber-Gordon, McGehee, and co-researchers used electric force microscopy (EFM) in conjunction with standard conductance measurements to map the location of voltage drops in CNT films (prepared using chemical vapor deposition) with current flowing through them. The researchers showed that the electrical performance and the voltage-drop maps can be drastically different for two devices even when they were fabricated immediately adjacent to each other on the same CNT film, that is, with constituent CNT characteristics that are statistically identical. For one device, voltage decreased slowly between source and drain electrodes while in another device voltage drops precipitously at one location, indicating large, dominating local resistances in the latter but none in the former. Numerical simulations of the electrostatic potential and current flow were performed in order to better understand the source of these experimental results. In the simulations, tubes 4 μm in length were placed in random orientations until the desired density was reached. Using tube and junction resistivities of 13 kΩ/μm and 200 kΩ/junction, respectively, the overall resistance of the network of tubes was solved using a sparse matrix inverter available in commercial software. The average conductance for 300 random films (with densities varying between 0 and 0.75 $tubes/\mu m^2$) agrees with theoretical results for conduction through a two-dimensional system of percolating sticks. In addition, simulations of films just above the percolation threshold (0.48 $tubes/\mu m^2$) explain the experimental voltage-drop maps; the networks showing the highest conductance have current flowing along many parallel paths while the networks showing the lowest conductance have one or only a few conducting paths.

Taking into consideration published results on metallic-semiconducting nanotube junctions as well as the fact that most methods of carbon nanotube synthesis produce mixtures of metallic and semiconducting tubes, the researchers realized a relatively small number of metallic tubes can disrupt conduction through an otherwise robust semiconducting network. The researchers therefore modified their simulation by making a portion of the network tubes semiconducting, and were able to construct a phase diagram that describes the nature of a CNT film as a function of tube density and semiconductor fraction. CNT-FETs can be constructed from films in three regions in the phase diagram, but those FETs can operate by two different gating mechanisms, involving the potential barrier formed at the metal-semiconductor junctions or the unblocked semiconducting paths that connect source to drain.

The researchers said, "Enriching the population of semiconducting tubes to 90% or more, which has become possible in the past few years, may produce FETs with a different gating mechanism and perhaps dramatically better characteristics than those made with more common 67% to 75% semiconducting mixes. Further characterization of field-modulated transport between metallic and semiconducting tubes, or through semiconducting tubes crossed by metallic tubes, will be important in determining whether the predominantly semiconducting networks really are better."

STEVEN TROHALAKI

Polyferrocenylsilanes Enable NIL-Fabricated Magneto-Ceramic Composite Nanorod Arrays

Driven by the need for faster and cheaper memory, the computer industry has an insatiable appetite for improved magnetic data storage. Recently, K. Liu, S. Fournier-Bidoz, and G.A. Ozin of the University of Toronto and I. Manners of the University of Bristol have developed a magnetic material that has potential for next-generation data storage applications. The material combines the use of high ceramic yield polyferrocenylsilanes (PFSs) and nanoimprint lithography (NIL) to make ordered arrays of magnetic pillars. The researchers' technique allows them to select the dimensions of the PFS material using well-defined anodic aluminum oxide (AAO) templates.

In a recent issue of *Chemistry of Materials* (DOI: 10.1021/cm900164b; Web publication: April 6), the researchers describe their use of aluminum-backed AAO templates to imprint patterns into PFS at elevated temperatures (150°C). Once raised above its glass transition temperature, the polymer melt was able to infiltrate the AAO template. The research team found that the extent of template filling was dependent on the temperature ramping rate. Under fast ramping conditions (15°C/min), the polymer partially filled the template but was able to completely fill the channels under slower ramping conditions (2°C/min).

In order to form magnetic patterned ceramic features, the group melt-filled the AAO with polymer under N_2/H_2 (95%/5%) to avoid the formation of iron oxides. After cooling the template and removing the aluminum backing, the researchers heated the filled template to between 500°C and 800°C. They removed the AAO template by dissolution in NaOH to reveal the patterned magnetic ceramic material. Of the three PFSs studied, only the polymer containing the acetylenic substituent gave a high enough ceramic yield (85%) to provide shape retention.

At elevated temperatures, pyrolysis of PFS forms α-Fe nanoparticles that have a theoretical domain size of 14 nm. The researchers found that they were able to tune the magnetic properties of the particles by varying the diameter of the AAO template. When pyrolyzed in templates with 55 nm pores, the resulting particles had an average size of 8.2 nm ± 2.4 nm and exhibited superparamagnetic behavior; whereas, polymer pyrolyzed in templates with 95 nm pores resulted in particles with average diameters of 20.9 nm ± 4.9 nm and exhibited ferromagnetic behavior. The group hypothesizes that the "growth of the nanoparticles was confined by the diameter of the nanochannels."

KEVIN P. HERLIHY

Confocal Annular Aperture Microscopy and NAIL Allow High Lateral Resolution in Backside Imaging of Integrated Circuits

Optical methods for detection of defects in silicon integrated circuits (IC) typically rely on light at wavelengths greater than 1 µm, where silicon is relatively transparent, which limits the lateral resolution to ~1 µm. F.H. Koklu, B.B. Goldberg, and M.S. Ünlü from Boston University, and S.B. Ippolito from the IBM Semiconductor Research & Development Center in Hopewell Junction, New York, achieved a better imaging resolution by combining a confocal laser scanning microscope with a silicon numerical aperture increasing lens (NAIL). A silicon NAIL placed on the backside of a silicon substrate effectively transforms it into an integrated solid immersion lens with increased numerical aperture (NA) of a factor of the square of the refractive index to a maximum of 3.5, the refractive index of silicon. Confocal laser scanning microscopes yield a lateral spatial resolution determined by the spot size of the laser beam. By combining the two techniques in conjunction with angular spectrum engineering, the researchers achieved a lateral spatial resolution of 145 nm at λ_0 = 1.3 µm, which represents a resolution of ~$\lambda_0/9$, as they reported in the April 15 issue of *Optics Letters* (DOI: 10.1364/OL.34.001261; p. 1261).

The confocal microscopy setup the researchers developed is a single-path, reflection-mode fiber-optical scanning microscope that uses a single mode fiber-coupled laser diode emitting at 1.3 µm and a 2 × 2 optical coupler. The researchers coupled the light in and out the single mode fiber with a collimating objective with matching NA and illuminated the sample and the NAIL using a second objective with NA = 0.26, the same objective that collected the reflected signal. The NAIL consisted of an undoped silicon hemisphere with radius of 1.61 mm. The images were generated by scanning the sample with the NAIL using a piezo translation stage. The researchers controlled the polarization direction of the incoming light with a half-wave plate located before the imaging objective. They modified the angular spectrum by blocking the center of the optical path in front of the imaging objective in such a way that they formed an annular aperture of variable inner radius. With this setup, they scanned an IC fabricated in a 0.35 µm process with 4 metal layers and 2 polysilicon layers deposited on a silicon substrate. The silicon substrate was thinned to a thickness of 458 µm ± 2 µm in order to optimize the resolution and imaging quality of the combined imaging approach. The structures imaged were passive calibration structures embedded into the first polysilicon layer.

The researchers were able to demonstrate that by tailoring the angular spectrum with an annular aperture while using linearly polarized illumination it was possible to significantly improve the spatial resolution in one direction. The research team achieved a record lateral spatial resolution of 145 nm in the direction perpendicular to the polarization direction of the incoming light for one-photon excitation schemes by engineering the pupil function. The researchers said that together with its contribution to longitudinal localization, angular spectrum tailoring proved to be a powerful and simple technique to improve the optical inspection of ICs.

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