Ultrabroadband Light Source Helps Pinpoint Structure of Organic Semiconductors

Organic semiconductor materials — used to make photovoltaic cells, LEDs and similar devices — can be quickly and efficiently made but often have surfaces composed of both amorphous and crystalline material states. They would perform better if they were completely crystalline, however, because the charges that flow through a semiconductor do not move as readily through amorphous material.

According to scientists at Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie in Berlin, at Carl von Ossietzky Universität in Oldenburg, Germany, and with UL-TRAS-CNR-INFM at Politecnico di Milano in Italy, optimizing organic semiconductors requires knowledge of the arrangement of the amorphous and crystalline portions, or domains.

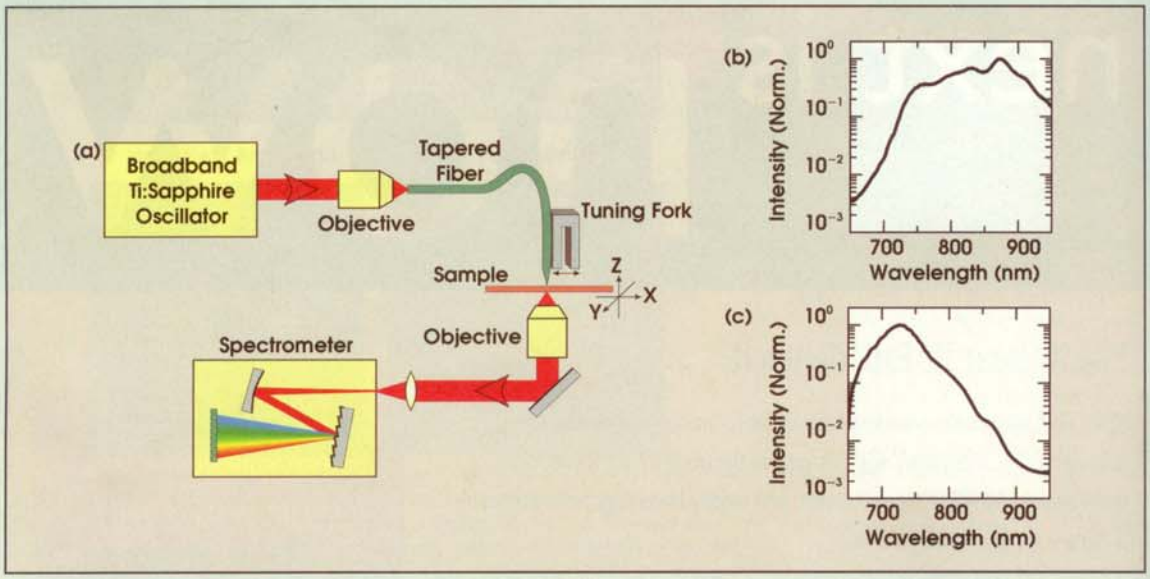
Atomic force microscopy can help visualize such domains by distinguishing differences in height, but it cannot provide chemical information and, therefore, cannot tell amorphous from crystalline. Optical spectroscopy, on the other hand, can elucidate the chemical differences but does not offer the spatial resolution necessary to pinpoint where domains of crystalline material separate from the amorphous ones.

Absorption spectra

The researchers, led by Christoph Lienau in Germany and Giulio Cerullo in Italy, reasoned that near-field scanning microscopy, which uses a nanometer-scale aperture and raster scanning to develop images that are unconstrained by the diffraction limit, would improve their results. However, the technique typically uses an incoherent light source, which does not provide the throughput that they required. Therefore, they used a Ti:sapphire oscillator made by Femtolasers Produktions GmbH of Vienna, Austria, as the light source.

"The combination of a broadband laser with a scanning near-field microscope allowed us to develop a near-field spectrometer able to measure local optical absorption spectra over an unprecedented 100-nm spatial scale," said Cerullo, an associate professor in the physics department at Politecnico di Milano.

The investigators used the near-field spectrometer to image thin films of oxotitanyl phthalocyanine (TiOPc), a material that has promising photovoltaic properties. During formation, TiOPc begins as an amorphous material, then becomes more crystalline in the presence of a solvent, such as tetrahydrofuran.



Investigators combined a Ti:sapphire and a near-field scanning microscope (NSOM) setup to obtain 100-nm resolution in spectrographic analysis of thin-film organic semiconductors (a). The tuning fork regulates the distance between the sample and the NSOM tip. The spectrum generated by the oscillator (b) and that transmitted through the NSOM's aperture (c) are shown. Images reprinted with permission of the American Chemical Society.

Conversion stops when the solvent is removed, permitting control over the electronic properties of the semiconductor.

They measured the spatially resolved absorption spectra of a partially converted TiOPc film, noting that it showed high absorption at ~720 nm, which was the amorphous phase's peak, but exhibited less absorption at ~845 nm, the crystalline phase's peak.

Importantly, they found that their observations of phase patterns corresponded well with those observed with far-field imaging, but did so at a length scale below the optical resolution. They also noted that both phases had some domains that were several hundred nanometers across, which indicates that photovoltaic devices made with the material could be optimized through the deposition or phase-conversion processes.

According to Lienau, now a professor in the physics department at the University of Oldenburg, the scientists are working on further improvements to the technique; for example, by using apertureless near-field scanning microscopy, which may improve the spatial resolution to 10 nm, and by using a coherent white-light source, such as a photonic crystal fiber, to extend the broadband wavelength range even further. □

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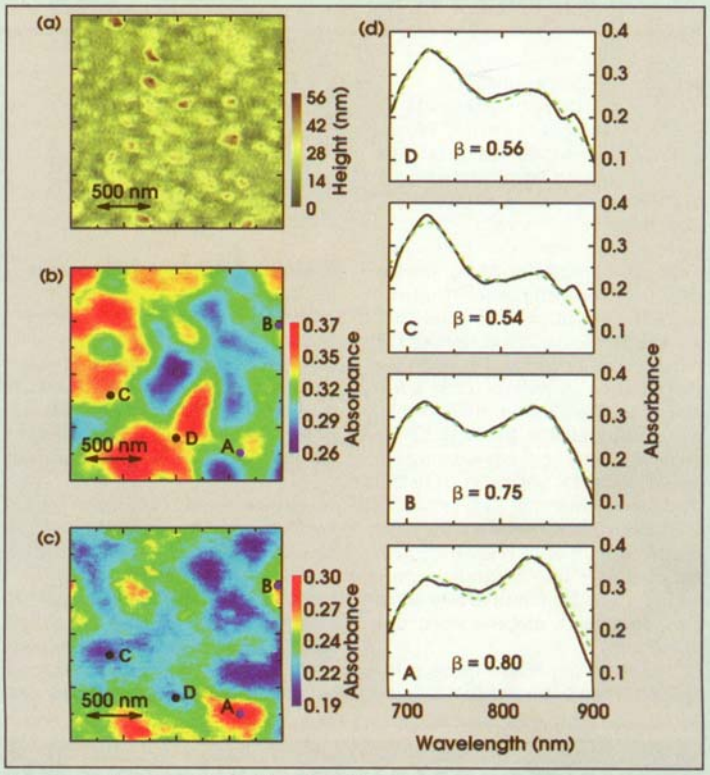

A topographical map of a thin film of oxotitanyl phthalocyanine (TiOPc) with mixed crystalline and amorphous domains (a) is shown in comparison with optical absorbance maps in the 700- to 750-nm (b) and 820- to 900-nm (c) ranges of the same area. Near-field absorption spectra for various positions (d, A-D) indicate which spots are amorphous and which are crystalline domains. Solid lines are the measured spectra; dashes represent model calculations; and β = the crystalline phase molar fraction.

A Crane for Very Small Construction Sites

It is always best to have the right tool for the job at hand. Unfortunately, researchers investigating the high-resolution positioning of single nanoparticles have lacked the proper equipment. As a result, they have not been able to controllably integrate a definite number of nanoparticles in circuits and quantum dots.

Now scientists from Shanghai Institute of Applied Physics in China have demonstrated single-particle dip-pen nanolithography (SP-DPN), a technique that provides the precise particle placement that researchers have been missing.

"SP-DPN can deposit different kinds of functional individual nanoparticles onto a desired position to form an accurate nanofeature," said professor Jun Hu.

Moving nanoparticles

Previously, investigators have manipulated an atomic force microscope (AFM) to laboriously push or pull nanoparticles across a flat surface, taking several hours to move a particle a distance of ~100 µm. In addition, they have not been able to transfer nanoparticles easily from one surface to another or to deal with the vertical dimension.

Suggested solutions have included the use of a charged AFM tip or substrate, but this scheme will not work if the nanoparticles are nonconductive. Light-based manipulation — such as optical tweezers — will not work for particles measuring only a few nanometers across. In dip-pen nanolithography, a coated AFM tip writes a pattern of molecules on a surface. Because of the tip inking, however, this approach is not suitable for single-particle work.

SP-DPN, on the other hand, is. Normally, an AFM tip is scanned across a surface in tapping mode, with the cantilever that bears the tip vibrating up and down at a resonant frequency. As the tip interacts with the surface, frequency changes are