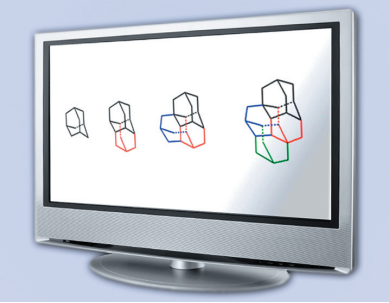
SCIENCE@BERKELEY LAB

October 11, 2007

Diamondoids: The Future on Display

Lynn Yarris, lcyarris@lbl.gov



Diamondoids are hydrocarbon molecules whose carbon-carbon cage structure is that of a diamond crystal. The simplest diamondoid is adamantane, which consists of a single cage, followed by diamantane with two cages, triamantane, tetramantane, and so on. The unusual optoelectronic properties of diamondoids include negative electron affinity, making them candidates for the kind of field-emission devices used in flat-panel screens.

Flat-panel TV enthusiasts are awaiting the day when field-emission devices (FEDs) based on nanosized electron emitters can replace current liquid-crystal display and plasma technologies. FEDs hold forth the promise of sharper images, wider fields of view, and substantially lower power consumption. Techno-pundits have predicted that carbon nanotubes will serve as the electron emitters for FED technology, but there's a new kid on the block—diamondoids!

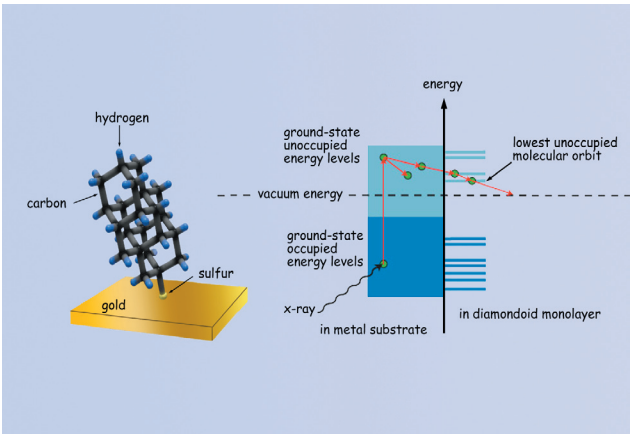
A study led by researchers at Berkeley Lab and Stanford University has provided the first experimental demonstration that diamondoids, which are nanometer-sized molecules that feature diamond-crystal cage structures—and are also known as cage hydrocarbons—can be excellent electron emitters, potentially superior to carbon nanotubes for FEDs.

"Our results showed that certain diamondoid self-assembled monolayers, when grown on metal substrates, yield the sharpest energy distribution peaks among all the electron emitters previously studied," says Wanli Yang, a physicist at Berkeley Lab's Advanced Light Source (ALS). Yang, with ALS scientist Zahid Hussain and Stanford physicist Zhi-Xun Shen, headed the multi-institutional collaboration that conducted the study.

The collaborators studied the electron-emission properties of a tetramantane diamondoid, one consisting of four diamond cages, on substrates of both gold and silver, using x-rays from ALS Beamline 10.0.1 and analytical techniques that included photoemission spectroscopy.

Like all diamondoids, the outer surfaces of the tetramantane's carbon cages feature dangling chemical bonds that are terminated by hydrogen atoms. To improve the functionality of their diamondoids and enable them to self-assemble in monolayers, collaborators modified the tetramantane by replacing one of the hydrogen atom terminators with a thiol group (a molecule with a sulfur-and-hydrogen-atom tail) then grew the modified tetramantanes into self-assembled monolayers.

A tetramantane fitted with a thiol tale, left, forms the unit of a monolayer on a metal substrate. The diagram at right illustrates how a monolayer of such diamondoids on metal absorbing x-ray photons leads to the monochromatic emission of electrons. An electron (green) in the metal substrate absorbs an x-ray (black wavy line) and is promoted to an excited state. The electron then loses energy within the metal, exciting other electrons, some of which are transferred to unoccupied energy levels in the diamondoid monolayer (far right). Further energy loss may take place within the monolayer before the electrons reach the lowest unoccupied molecular orbital (LUMO). Since the LUMO has higher energy than the vacuum (dashed line), the electrons are emitted with an energy equal to the difference between the LUMO and vacuum energies.



continued

“For the monolayer diamondoids grown on silver, 68 percent of all emitted electrons were within a single energy peak of about 0.5-electron-volt width,” says Yang. “This monochromatic emission is several times stronger than that reported for bulk diamond surfaces, which means much more electrons were emitted at the same speed, a very desirable property for use in FEDs.”

It was also a good sign for their potential application in FEDs that the diamondoids could be purified and functionalized with precise control and could be induced to self-assemble in uniform monolayers over a large area. These attributes help make diamondoids far more suitable for commercial-scale manufacturing and device reproduction than carbon nanotubes, which are notoriously heterogeneous, expensive, and hard to purify.

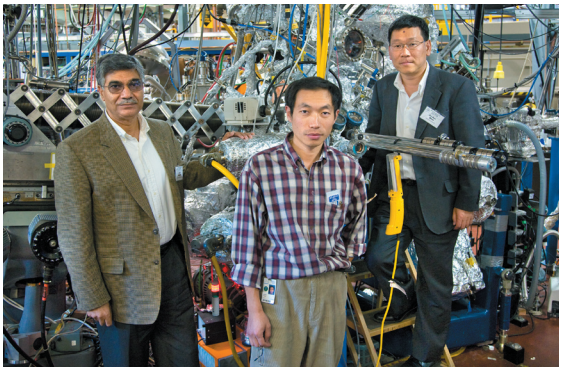
Diamondoids were originally discovered and isolated from petroleum in 1933. The first and simplest diamondoid was named adamantane, from the Greek word for diamond, because its cage-like structure could be superimposed upon a diamond lattice. Their cagelike structure and hydrogen-terminated surfaces endow diamondoids with a unique optoelectronic property called negative electron affinity (NEA). Essentially, this means that conduction electrons have higher energies inside the diamondoid than out, causing them to fly out of the cage even in the absence of any “turn-on” bias voltage.

“Because the conduction electrons have a higher energy level than the energy level at vacuum, they will spontaneously emit from the cage to reach the lower energy level,” explains Yang. “This low or zero turn-on voltage is very important because it is directly related to the efficiency, noise level, and functional lifetimes for diamondoids as electron emitters.”

The collaborators tested several different samples, with bias voltages ranging from zero to nine volts. Their results indicated that the diamondoid molecule itself, the thiol group, the single monolayer, and the substrate all played crucial roles in generating the observed NEA phenomenon.

Explained Shen, “The ALS’s x-ray excited electrons go through a scattering process and accumulate at a certain lowest unoccupied molecular orbital, or LUMO. According to the scenario of NEA, the LUMO for diamondoid is higher than that for vacuum, so the accumulated electrons all are emitted at an energy equal to the energy differences between LUMO and vacuum, which leads to the peak in the photoemission spectrum.”

The modification of diamondoid molecules with other functionalizing compounds besides a thiol group could open the door to further optoelectronic and other unique properties, and perhaps to capabilities not possible with carbon nanotubes. FEDs based on diamondoid electron emitters could see widespread commercial use beyond flat-panel TV displays, for example in the microwave telecommunications and microelectronics industries. Scientific applications also stand to benefit greatly, such as electron beam lithography, electron microscopy, and next-generation free electron lasers.



Zahid Hussain, Wanli Yang, and Z.-X.Shen used undulator Beamline 10.0.1 at Berkeley Lab’s Advanced Light Source to provide the first experimental evidence that diamondoids can be excellent electron emitters, potentially superior to carbon nanotubes for field-emission devices.

“There is much work to be done before diamondoids can be incorporated into commercial devices, but compared to the extensive research efforts that have gone into carbon nanotubes in the past decade, not much technological effort has even started on diamondoids,” said Yang. “We really don’t want to miss out on these fascinating new members of the carbon family.”

Other members of the diamondoid collaboration were Norman Mannella, Kiyohisa Tanaka, and Xingjiang Zhou of both Berkeley Lab and Stanford; Nick Melosh, Jason Fabbri, Mike Kelly, and Worawat Meevasana of Stanford; Peter Schreiner, Andrey Fokin, Natalie Fokina, and Boryslav Tkachenko of the University of Giesen and the Kiev Polytechnic Institute; Jeremy Dahl and Robert Carlson of Molecular Diamond Technologies; and Trevor Willey, Jonathan Lee, and Tony van Buuren of Lawrence Livermore National Laboratory. Don Paul, Chief Technology Officer for Chevron, helped initiate this collaboration.

continued

Additional information

"Monochromatic electron photoemission from diamondoid monolayers," by W. L. Yang, J. D. Fabbri, T. M. Willey, J. R. I. Lee, J. E. Dahl, R. M. K. Carlson, P. R. Schreiner, A. A. Fokin, B. A. Tkachenko, N. A. Fokina, W. Meevasana, N. Mannella, K. Tanaka, X. J. Zhou, T. van Buuren, M. A. Kelly, Z. Hussain, N. A. Melosh, and Z.-X. Shen, appeared in the 8 June 2007 issue of *Science* and is available online to subscribers at http://dx.doi.org/10.1126/science.1141811.

More about Z.-X.Shen's research is at http://www.stanford.edu/group/arpes/index.html.

More about Berkeley Lab's Advanced Light Source is at http://www-als.lbl.gov/.