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Conductivity is More Than Skin Deep

Getting Beneath the Surface Reveals a Breakthrough in Solar Cell Material

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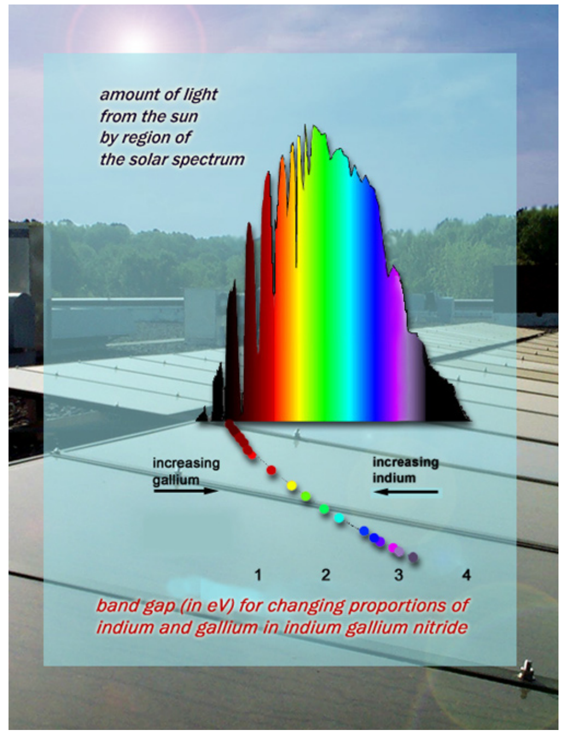
A team of researchers from Berkeley Lab's Materials Sciences Division (MSD), led by Wladek Walukiewicz and working with colleagues from Cornell University, has made a form of the semiconductor indium nitride that can conduct positive charges. For any other semiconductor the news would be unremarkable. But indium nitride is one of the most frustrating, if most promising, of semiconductor materials.

In 2002 Walukiewicz and his colleagues discovered that indium nitride has a remarkably narrow band gap, only 0.7 electron volts, which corresponds to the near-infrared region of the electromagnetic spectrum. Gallium nitride, another group III nitride (elements in group III of the periodic table have three valence electrons), has a band gap of 3.4 electron volts, matching the near-ultraviolet region of the spectrum. Layers of indium, gallium, and nitrogen alloyed in different proportions could be stacked in a solar cell that, spanning virtually the entire spectrum of sunlight, would be far more efficient than any yet made.



The narrow band gap of indium nitride corresponds to the infrared end of the solar spectrum; the wide band gap of gallium nitride corresponds to the ultraviolet end. Alloys of the two compounds could be combined to make a full-spectrum solar cell.

When electrons get in the way

What makes indium nitride frustrating, however, is that most semiconductor devices require two types of the material to form a junction, an n-type that conducts negatively charged electrons and a p-type that conducts positively charged "holes." These types are usually made by doping the native material with impurities, either elements that donate electrons or those that accept electrons and leave behind holes.

"Indium nitride is unique; it likes to be n-type," says Walukiewicz. Not least because its peculiar electronic structure requires an unusual amount of energy to move the electrons out of its conduction band and make way for holes. Even native, undoped InN is n-type—and it has proved almost impossible to make the p-type. Until now.

The reason is that indium nitride crystals are riddled with defects, as many as tens of billions per square centimeter, and lots of atoms in these defects are unable to form bonds with their absent neighbors. What makes InN unique is that the energy level of these defects lies right in the middle of InN's conduction band, so the dangling bonds are all too eager to donate spare electrons to the conduction band.

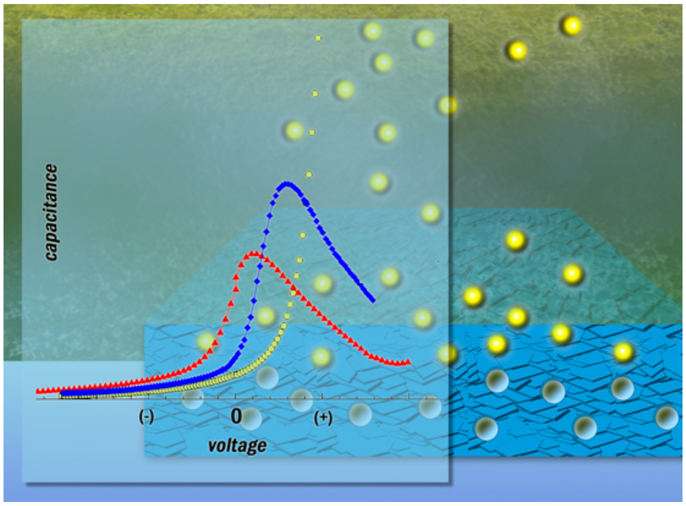
Moreover, says MSD team member Joel Ager, "Dangling bonds are found on the surface of indium nitride, where they create an n-type accumulation layer impervious to chemical or physical treatment."

The result, says team member Kin Man Yu of MSD, "is that you can't make an electrical contact with the bulk of the material, below the surface. Even if the bulk was p-type, you can't reach it because you can't get past the n-type surface layer."

Reaching into the interior

Nevertheless, it should be possible to positively dope InN with an acceptor element. Magnesium has one less valence electron than indium and readily accepts electrons, leaving behind positively charged holes.

Using molecular beam epitaxy, William Schaff and his associates at Cornell University made samples of magnesium-doped indium nitride and sent them to Berkeley Lab. The challenge was to prove that the magnesium atoms had created p-type material in the bulk of the InN—even though the charge was masked by the negative surface accumulation layer.



Because of the persistent surface accumulation of electrons, solid electrodes can't make contact with the bulk. But with increasing voltage a liquid electrolyte can remove enough surface electrons to sense holes in the bulk. Red and blue lines are samples of magnesium-doped InN; yellow line is undoped InN. Rising slopes indicate negative charge; declining slopes indicate the positive charge of holes in the bulk of the doped material.

"A common method of measuring charge in a semiconductor is watching how the capacitance changes with changes in voltage," Ager says. "To make such a measurement of bulk InN, we had to get rid of the n-type layer."

Says Walukiewicz, "We would have needed a huge electric field" to do this the normal way, with a metal electrode. "It occurred to us we could use a liquid electrode—an electrolyte—instead."

They formed a contact between their samples and a sodium hydroxide solution. "As we increased the voltage, it removed electrons from the surface and gave us access to the bulk," Walukiewicz says. "We were able to see evidence of holes below the surface layer, beginning about six nanometers down."

Yet, says Ager, "we knew that skeptics would demand additional verification." By irradiating the doped samples with energetic alpha particles the researchers created additional defects in the bulk of the p-type material, which donated more electrons and effectively filled the holes created by the magnesium impurities. Eventually the electrical activity of the magnesium acceptor atoms was overwhelmed, and the samples began to resemble indium nitride that had never been doped.

Photoluminescence—light emission after exciting the samples with a laser—also changed with step-wise increases in the radiation dose, as holes in the doped samples were displaced by electrons.

Ager says, "Proving that our doped samples were p-type is a major step forward. But plenty of challenges remain." Berkeley Lab researchers and their collaborators were first to establish the potential of group III nitrides and first to see the promise of indium gallium nitride alloys, but several other groups offer serious competition in the race to achieve practical applications.

"We're optimistic," Walukiewicz says. "Otherwise we wouldn't be doing this."

Members of the team reporting p-type doping of indium nitride include Kin Man Yu, Wladek Walukiewicz, and Joel Ager of Berkeley Lab's MSD, Becca Jones, Sonny Li, and Eugene Haller of MSD and the University of California at Berkeley's Department of Materials Science and Engineering, and Hai Lu and William Schaff of Cornell University's Department of Electrical and Computer Engineering.

This is an edited version of an article appearing in the May, 2006 edition of Science@Berkeley Lab, the online science magazine of Lawrence Berkeley National Laboratory. The full-length version, including links to further information, may be accessed at http://www.lbl.gov/Science-Articles/Archive/sabl/2006/May/01-conductivity.html.