Local vibrational modes of impurities in semiconductors

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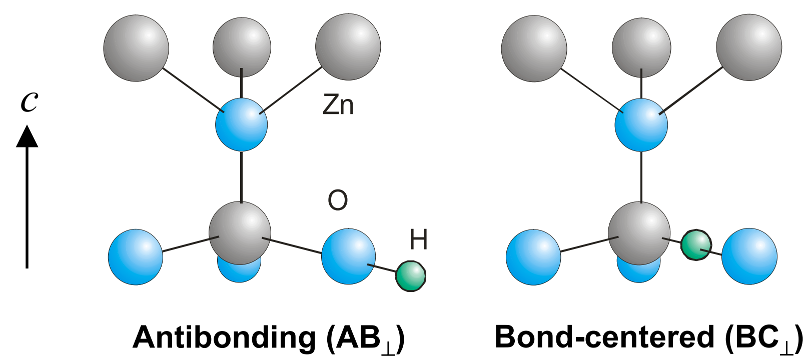
• Zinc oxide (ZnO) is a *wide-bandgap* semiconductor that has attracted tremendous interest as a blue light-emitting material and a material for transparent transistors. As grown, however, ZnO is almost always *n* type, while *p*-type conductivity has been elusive. A fundamental understanding of donors in ZnO will contribute to the development of *p*-type material.

• Recent theoretical work (Van de Walle) predicted that hydrogen impurities act as shallow donors. To determine the structure of these donors, we used infrared (IR) spectroscopy to measure the *local vibrational modes* of ZnO annealed in hydrogen. Our measurements confirmed that hydrogen attaches to a host oxygen atom. Electrical results showed that hydrogen acts as a shallow donor.

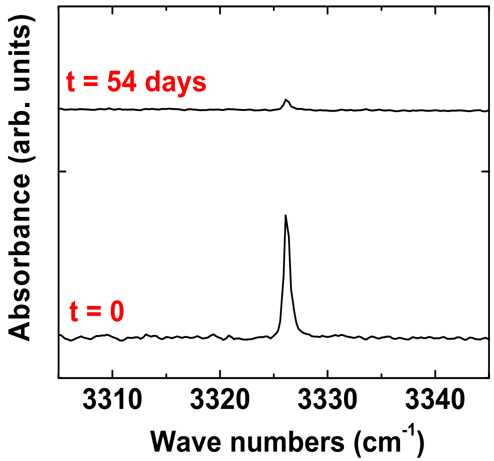
• Surprisingly, the complexes are unstable. After several weeks, the O-H complexes decay, perhaps forming H_2 molecules.

• Future work will further investigate the decay and formation of hydrogen donors. We will also explore novel approaches to achieve *p*-type doping, an important goal for ZnO-based devices.

Appl. Phys. Lett. **81**, 3807-9 (2002).



Two proposed models for oxygen-hydrogen (O-H) complexes in ZnO.



IR spectra of O-H complexes at liquid-helium temperatures. After several weeks, the peak disappears, suggesting the formation of H_2.

Aim of the project:

Zinc oxide (ZnO) is a semiconductor that has attracted tremendous interest as an important electronic material for a range of applications. A *wide-bandgap* semiconductor, ZnO emits light in the blue-to-ultraviolet region of the spectrum. The efficiency of the emission is higher than more conventional materials, making ZnO a strong candidate for energy-efficient white lighting. ZnO is also used in transparent transistors, “invisible” devices which could be very useful in products such as liquid-crystal displays. Unlike many other compound semiconductors, ZnO is extremely cheap and environmentally friendly.

In spite of its numerous advantages and potential applications, ZnO suffers from one major drawback: as grown, it contains a high level of *donor impurities*. These impurities donate free *electrons*, making ZnO *n*-type. Reliable *p*-type doping, where current is carried by free *holes*, has not been achieved. The lack of *p*-type conductivity has prevented ZnO from competing with other wide-bandgap semiconductors. In order to overcome that obstacle, the role of donor impurities in ZnO must be understood. In our NSF-sponsored research, we are investigating the properties of hydrogen donors in ZnO.

Research Results:

Recent theoretical work (Van de Walle) has demonstrated that hydrogen is a shallow donor in ZnO that may be introduced into the bulk during growth or processing. In the first figure, two proposed models for hydrogen donors are shown. In one model, hydrogen is in the *antibonding* orientation, attached to a host oxygen atom and pointing away from the Zn-O bond. Another model is the *bond-centered* configuration, where the hydrogen sits between the host Zn and O. In order to determine the structure and stability of hydrogen donors experimentally, we used infrared (IR) spectroscopy to measure the *local vibrational modes* arising from these complexes. In this technique, IR light is absorbed by an O-H complex, causing the hydrogen atom to vibrate. Hydrogen was diffused into nominally undoped ZnO crystals by annealing in hydrogen gas.

IR spectra of ZnO annealed in hydrogen are shown in the second figure. An absorption peak is observed at a vibrational frequency of 3327 cm^{-1}, in good agreement with an O-H bond-stretching mode. Samples that are annealed in deuterium show the expected isotope shift for O-D complexes. The appearance of the IR absorption peak is correlated with an increase in free electron concentration, proving that this complex is, indeed, a shallow donor. Polarized IR experiments have shown that the hydrogen is not aligned along the *c* axis, but rather at a tetrahedral angle, as shown in the figure. The observed frequency, however, is consistent with the antibonding *and* bond-centered models. Ongoing experiments utilizing high pressures will enable us to discriminate between these two models.

Surprisingly, we found that the O-H complex is unstable at room temperature. As shown in the second figure, after a few weeks, the peak intensity decreases substantially. It is possible that the hydrogen forms H_2 molecules, which have essentially no IR signature. Electrical measurements show a corresponding decrease in electron concentration, which is consistent with the formation of neutral H_2 molecules.

Conclusions and significance:

A fundamental understanding of donors in ZnO will contribute to the eventual development of *p*-type ZnO. In this work, we have observed hydrogen donors experimentally, and proposed a model for their structure. Given the omnipresence of hydrogen in growth and processing of semiconductors, characterizing the properties of hydrogen in ZnO is an important goal. Toward that end, the kinetics of hydrogen formation and decay will be investigated in detail. Future studies will also focus on interactions of hydrogen with *p*-type dopants and novel methods for achieving *p*-type conductivity in ZnO. One promising approach to produce *p*-type material involves the implantation of nitrogen atoms into ZnO, followed by pulsed laser annealing (PLA). This method has been used successfully in other semiconductors such as gallium arsenide. In ZnO, it is hoped that the PLA technique will result in high nitrogen acceptor concentrations with relatively few compensating donors.

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Education:

This NSF-sponsored research has supported two undergraduates (John Singleton and Lance Culnane), three Ph.D. students (Slade Jokela, Win Maw Hliang Oo, and Kirill Zhuravlev), and one visiting scientist (Leonardo Hsu). This grant has also sponsored the development of upper-division solid state lecture demonstrations.

Thermal conductivity lecture demonstration

Outreach:

The PI has organized visits by kids from the Washington State University Children's Center (ages 2-10) and visited a local elementary school (grades K-6). He was also a mentor for a high school senior project on building a Tesla Coil.

The PI demonstrating an electromagnet to kids at a local elementary school.