Abstract

Zinc oxide (ZnO) is a wide-band gap semiconductor that has attracted resurgent interest as an electronic material for a range of applications. In our work, we have focused on the properties of hydrogen donors in ZnO. In bulk, single-crystal ZnO doped with hydrogen or deuterium, infrared (IR) absorption peaks corresponding to O–H and O–D stretch modes were observed at 3326.3 and 2470.3 cm$^{-1}$, respectively, at liquid-helium temperatures. IR spectroscopy using polarized light showed that the O–H dipoles are aligned along an angle 111° to the c-axis. The slight negative shift of the O–H mode as a function of hydrostatic pressure suggests that the hydrogen resides in an anti-bonding orientation. The O–H complexes are unstable, perhaps due to the formation of “hidden” H$_2$ molecules. As dimensions approach the nanoscale, the vastly increased surface-to-volume ratio leads to interesting phenomena. At moderate annealing temperatures (350°C), hydrogen interacts with the nanoparticles, resulting in a dramatic increase in electrical conductivity, free-carrier absorption, and IR reflectivity.

1. Introduction

Zinc oxide (ZnO) is a wide-band gap semiconductor that has attracted much interest as a material for numerous electronic and optoelectronic applications [1]. ZnO emits light in the blue-to-UV region of the spectrum. The quantum efficiency is reportedly higher than other materials such as GaN [2], making ZnO a strong candidate for energy-efficient lighting applications. In addition, unlike GaN, large single crystals can be grown [3]. ZnO is used as a transparent conductor material [4] in solar cells [5] and is a promising material for transparent transistors, devices which could be used in a variety of consumer products [6].

Despite its advantageous materials properties, ZnO tends to contain a large concentration of donor impurities. These donors compensate acceptors and/or give free electrons to the conduction band, preventing p-type conductivity. Reliable p-type doping has not been achieved. The lack of p-type material has prevented ZnO from realizing its potential as a useful material for devices. In order to solve that significant problem, it would be extremely beneficial to know the role of donor impurities in ZnO. In our work, we have investigated the properties of hydrogen donors.

Several decades ago, Mollwo [7] and Thomas and Lander [8] showed that hydrogen could diffuse into ZnO and increase the n-type conductivity. More recently, first-principles calculations by Van de Walle [9] showed that hydrogen could be an important shallow donor in ZnO, and several microscopic models were proposed. Motivated by the work of Van de Walle, experiments on muonium in ZnO [10] and electron-nuclear resonance measurements on as-grown, n-type ZnO [11] gave support to the idea that hydrogen could act as a shallow donor.

To elucidate the microscopic structure of hydrogen donors, infrared (IR) spectroscopy was performed to detect local vibrational modes (LVMs) arising from these complexes [12]. Although it was clearly demonstrated that hydrogen forms O–H complexes, the actual structure of these complexes was not known. Two proposed models for
the O–H donors are shown in Fig. 1, denoted the antibonding (AB) and bond-centered (BC) configurations. In both of these models, the O–H bond lies at a (nearly) tetrahedral angle to the c-axis. Theoretical studies also proposed AB1 and BC configurations, in which the O–H bond lies parallel to the c-axis (not shown). Since the predicted LVM frequencies for all of the models are similar, further experiments were performed to pinpoint the most likely structure.

Most of the results in this article are based on Refs. [12–14]. Recent work by Seager and Myers [15], Nickel and Fleischer [16], Lavrov et al. [17,18], and Halliburton et al. [19] have also reported hydrogen-related LVMs in ZnO. However, the frequencies of those modes are different from the frequencies that we observed, perhaps due to sample variations.

2. Experiment

In this work, single crystal, c-cut ZnO samples from Cermet, Inc., with a thickness of 0.5 mm, were used. For hydrogen diffusion, samples were sealed inside a quartz ampoule, evacuated and then backfilled with 2/3 atm of H2. The ampoule was placed in a horizontal furnace and annealed at temperatures around 700–800°C for several hours. Then, the ampoule was rapidly cooled to room temperature by retrieving it from the furnace and dropping in water. After the hydrogen diffusion, the free-electron concentration increased by a factor of 2–3, to 4–5 × 1017 cm−3. The increase in free electrons is obviously consistent with the model that hydrogen is a shallow donor in ZnO.

Hall-effect measurements (MMR Technologies, Inc.) were performed in the van der Pauw geometry, using a 1 Tesla electromagnet. The as-received samples had a free-electron concentration of n~2 × 1017 cm−3. IR spectroscopy was performed using a Bomem DA8 Fourier transform IR (FTIR) spectrometer with a KBr beamsplitter and an InSb mid-IR detector. The O–H stretch mode was measured at room temperature (~300 K) and liquid-helium temperatures (~10 K). For the liquid-helium measurements, a Janis STVP continuous-flow cryostat with wedged ZnSe windows was used.

3. Results and discussion

Using IR spectroscopy, we observed O–H and O–D stretch modes at 3326.3 and 2470.3 cm−1, respectively, at liquid-helium temperatures. As the temperature is increased, the LVM width increases and the mode shifts to higher frequency (Fig. 2). The shift of the LVM frequency is modeled by

$$\delta v = \frac{\delta v_0}{\exp(hv/kT) - 1}.$$  

where h is Planck’s constant, k is Boltzman’s constant, and T is the temperature in Kelvin. In this model [20], the LVM is assumed to interact primarily with one phonon frequency (ν). The solid line in Fig. 3 is a fit to the data, using Eq. (1), with $\delta v_0 = 7$ cm−1 and $\nu = 100$ cm−1. The value of $\nu$ is physically reasonable, since there is a peak in the one-phonon density of states near 100 cm−1 [21].

These IR measurements were performed at normal incidence on c-cut ZnO samples. Therefore, it is clear that the observed O–H dipoles were not aligned parallel to the c-axis. This observation appears to contradict theoretical reports, which claim that the lowest energy orientation of the hydrogen is in the BC configuration [9]. In addition, a study of muonium in ZnO claimed that the complexes are aligned parallel to the c-axis [22].

To check our result, we performed polarized IR spectroscopy on an a-cut sample. For light that was
polarized along the c axis, the O–H absorption is reduced as compared to light polarized perpendicular to the c-axis. Our results are consistent with O–H dipoles that are aligned at an angle of \( \sim 111^\circ \) to the c-axis [23]. The polarized IR results are therefore in agreement with the \( \text{AB\text{\textperp}} \) or \( \text{BC\text{\textperp}} \) models.

In order to discriminate between the \( \text{AB\text{\textperp}} \) and \( \text{BC\text{\textperp}} \) models, we measured the O–H LVM as a function of hydrostatic pressure. High-pressure measurements were performed at liquid-helium temperatures, using a diamond-anvil cell. We found that there is only a very slight shift with pressure, approximately \(-1.8 \text{ cm}^{-1}/\text{GPa}\) [23]. Qualitatively, this small shift would seem to favor the \( \text{AB\text{\textperp}} \) orientation, in which the hydrogen is not crowded by neighboring atoms. According to first-principles calculations by Limpijumnong and Zhang [24], the O–H LVM should exhibit a positive shift if it is in a BC configuration and a negative shift if it is in an AB configuration. The observed negative shift is qualitatively consistent with the \( \text{AB\text{\textperp}} \) structure, although Limpijumnong and Zhang predicted a larger magnitude (\(-4 \text{ cm}^{-1}/\text{GPa}\)).

The O–H complexes are unstable at room temperature, decaying substantially after a few weeks. In order to quantify this decay process, two identical hydrogenated samples were prepared. The electron concentration was measured as a function of time for one sample, while room-temperature IR spectroscopy was performed on the other sample. The results of these measurements are shown in Fig. 4, where the circles and triangles refer to the electrical data and IR data, respectively.

It is clear that the decay of the IR peak and the reduction in free-electron concentration are very well correlated, demonstrating that the O–H complexes are indeed shallow donors. The data were fit using a bimolecular decay model [23], consistent with the idea that hydrogen donors may form \( \text{H}_2 \) molecules [25]. Since \( \text{H}_2 \) molecules are essentially IR inactive, and electrically neutral, the formation of \( \text{H}_2 \) molecules results in a decrease in the IR absorption peak and free-electron concentration.

As the dimensions of semiconductor crystals approach the nanoscale, the huge increase in surface-to-volume ratio should result in different impurity behavior. To explore this effect, we studied the effect of hydrogen impurities on the IR and electrical properties of ZnO nanoparticles. The nanoparticles were synthesized by standard wet-chemistry techniques ([26] and references therein). Transmission electron microscopy showed that the particles were roughly spherical, with an average diameter of \( \sim 15 \text{ nm} \). The nanopowder was pressed into pellets \( \sim 0.25 \text{ mm} \) thick. Samples were then annealed in hydrogen gas at a temperature of \( 350^\circ \text{C} \).

As shown in Fig. 5, the conductivity of the ZnO pellets increased by several orders of magnitude after hydrogenation. This increase in conductivity was accompanied by a large increase in free-carrier absorption (Fig. 6). Annealing in argon gas did not lead to such changes. These
In ZnO nanoparticles, at moderate annealing temperatures (350 °C), hydrogen causes a dramatic increase in electrical conductivity, free-carrier absorption, and IR reflectivity. These results could be relevant to hydrogen sensing and storage applications.

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