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HYDROGEN DONORS IN ZINC OXIDE

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Abstract: Zinc oxide (ZnO) has emerged as a leading material for micro- and optoelectronic applications. Although the fabrication of ZnO, from nanocrystals to bulk single crystals, is well established, a major roadblock for fabricating optoelectronic devices is the lack of reliable *p*-type doping. The presence of compensating donors inhibits the growth of *p*-type ZnO. In this paper, studies pertaining to the microscopic structure and doping properties of hydrogen in ZnO are described. Results from infrared (IR) spectroscopy are consistent with a model where the hydrogen attaches to a host oxygen atom, in an anti-bonding orientation, which is not aligned along the *c* axis. These hydrogen complexes are unstable, however, perhaps due to the formation of H_2 molecules.

Key words: ZnO, zinc oxide, IR, infrared, hydrogen, vibrational modes

1. INTRODUCTION

Zinc oxide (ZnO) has a wide range of industrial applications. An environmentally friendly, wide-bandgap semiconductor, ZnO may prove to be a valuable material for blue lasers and light-emitting diodes [1]. The lack of reliable *p*-type doping, however, is major roadblock to the realization of such devices. Compensating donors play a detrimental role in preventing *p*-type conductivity. Early work by Mollwo [2] and Thomas and Lander [3] showed that the diffusion of hydrogen into ZnO could increase the electrical conductivity. The more recent theoretical work by Van de Walle [4], which showed that hydrogen should be a shallow donor in ZnO, re-ignited interest in this subject. Subsequent experiments involving muonium in ZnO [5] and electron-nuclear double resonance (ENDOR) spectroscopy [6] verified that hydrogen is a shallow donor in ZnO. In this paper, we review results from infrared (IR) spectroscopy of hydrogen diffused into ZnO [7-9]. Preliminary Hall-effect and high-pressure results are also presented.

2. EXPERIMENTAL TECHNIQUES

Single crystal, *c*-cut ZnO samples were purchased from Cermet, Inc. Samples were sealed in quartz ampoules along with hydrogen or deuterium gas. In addition, ZnO powder was placed in the ampoule, in order to prevent the decomposition of the ZnO crystal due to hydrogen reduction. Hydrogen diffusion occurred at a temperature of 700-800°C for 10-100 hr, followed by a rapid quench to room temperature by immersion of the ampoule in water. The sample was then retrieved by breaking the ampoule.

IR spectra were taken at room temperature (300 K) and liquid-helium temperatures (5-15 K), using a Bomem DA8 Fourier transform infrared (FTIR) spectrometer and an InSb detector. For the low-temperature measurements, a Janis continuous-flow liquid-helium cryostat with wedged, IR-transparent windows was utilized. Hall-effect measurements, in the Van der Pauw geometry, were performed at room temperature using a system from MMR Technologies. Wires were attached to the ZnO using silver paint, which provided adequate Ohmic contacts for the electron concentrations (10^{17} cm^{-3}) in these samples.

3. RESULTS

3.1 IR spectroscopy and Hall-effect measurements

At liquid-helium temperatures, hydrogenated ZnO samples exhibit an O-H stretch mode at a frequency of 3326 cm^{-1} at liquid-helium temperatures (Fig 1). The IR peak corresponding to this mode broadens and shifts to higher frequency when the sample is warmed to room temperature. Deuterated ZnO samples, at liquid-helium temperatures, have an O-D stretch mode at 2470 cm^{-1} [7]. The ratio of the O-H and O-D frequencies are in good agreement with a simple diatomic model. More importantly, the frequency ratio is nearly identical to that of O-H and O-D complexes in GaP [10]. Our observed O-H mode is different from those observed by Lavrov *et al.* [11] and Nickel and Fleischer [12].

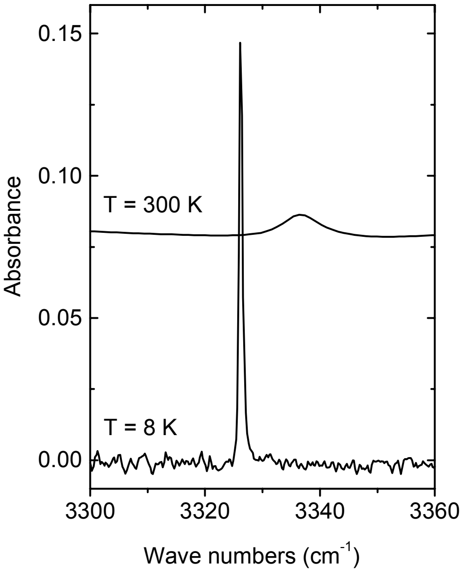

Figure 1. IR spectra of O-H complexes in ZnO, at room- and liquid-helium temperatures.

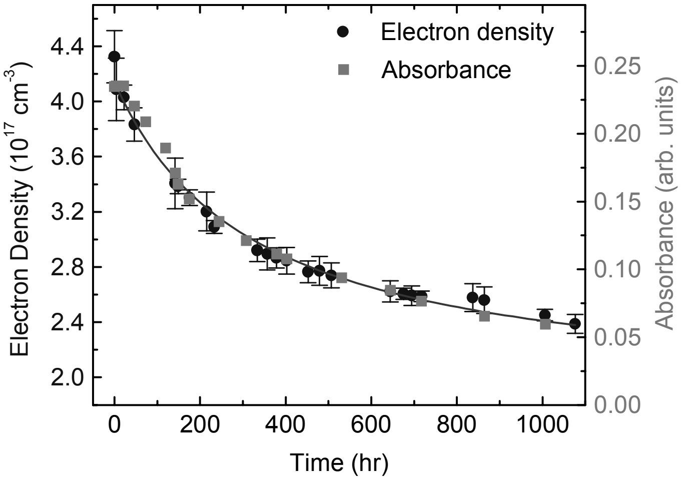

Figure 2. Electron density (circles) and IR absorbance of the O-H peak (squares) as a function of time, in hydrogenated ZnO.

At a temperature of 300 K, the O-H complexes are unstable. Over the course of a few months, the intensity of the IR peak decreases substantially. In order to quantify this decay process, we prepared two identical hydrogenated samples. For one sample, the electron concentration was determined as a function of time, using room-temperature Hall-effect measurements. For the other sample, room-temperature IR spectroscopy was used to measure the intensity of the O-H peak as a function of time. The results of these measurements are plotted in Fig. 2. The circles and squares refer to the Hall-effect and IR measurements, respectively.

In Fig. 2, there are two features worth noting. First, the decay of the O-H peak and the decay of the free-electron concentration are correlated, providing evidence that the O-H complexes are shallow donors. Second, the data were fit using a biexponential decay model,

$$N = \frac{1}{1/N_0 + At}, \tag{1}$$

where N is the number of O-H complexes, N_0 and A are adjustable parameters, and t is time. This model is consistent with the idea that hydrogen donors may form H_2 molecules [13]. Since H_2 molecules are essentially IR inactive, and electrically neutral, the formation of H_2 molecules results in a decrease in the O-H IR mode *and* free-electron concentration.

3.2 Polarized IR spectroscopy

The IR measurements described in the previous section were performed in a normal incidence geometry on *c*-cut ZnO samples. Since the polarization of the light is perpendicular to the *c* axis, it follows that the O-H complexes that we observed are *not* aligned along the *c* axis. This observation contradicts some theoretical reports, which claim that the lowest energy orientation of the hydrogen is parallel to the *c* axis [4]. The calculated energy differences are small, however, on the order of 0.1 eV.

To check this 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 perpendicular to the *c* axis. As discussed in Ref. 8, our results are consistent with O-H dipoles that are aligned at an angle of ~112 ° to the *c* axis.

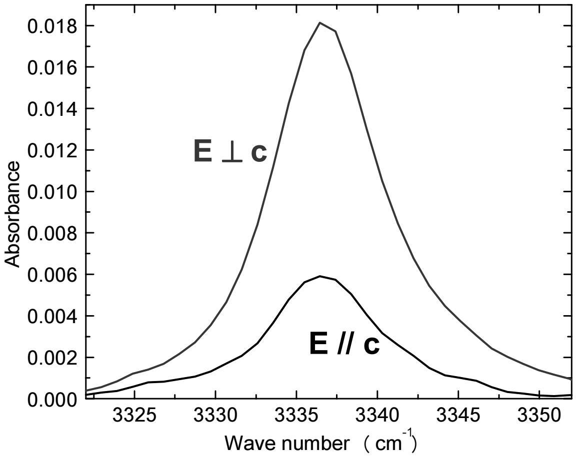

Figure 3. Polarized IR spectra of O-H complexes in ZnO, at room temperature.

3.3 High-pressure measurements

Regarding the structure of the O-H complexes, one question remains: is the configuration bond-centered or anti-bonding? Since both structures have identical symmetry, it is not obvious how to distinguish between them. One possible method involves measuring the O-H stretch-mode frequency as a function of hydrostatic pressure. By comparing the results with predictions of *ab initio* calculations, it should be possible to determine the structure with reasonable certainty.

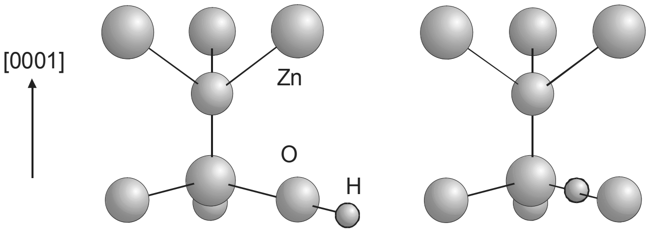

Figure 4. Ball-and-stick diagrams of the antibonding (left) and bond-centered (right) models for hydrogen donors in ZnO.

High-pressure measurements were performed at room temperature, using a moissanite-anvil cell. As shown in Fig. 5, there is only a very slight shift with pressure, approximately -1 cm^{-1}/GPa. Qualitatively, this small shift would seem to favor the antibonding orientation, in which the hydrogen is not crowded by neighboring atoms. However, it will be necessary to compare our results with first-principles calculations. In addition, IR measurements over a larger range of pressures will be performed.

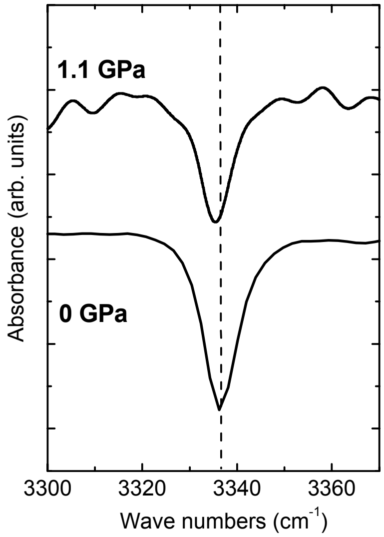

Figure 5. IR spectra of hydrogenated ZnO, at room temperature, at hydrostatic pressures of 0 and 1.1 GPa.

4. UNSOLVED MYSTERIES

In addition to the bond-centered versus antibonding question, there are two results that do not have good explanations. First, as shown in Fig. 6, hydrogenated samples from Cermet show a much stronger peak than identically treated samples from Eagle-Pitcher. This may be due to a higher concentration of oxygen vacancies in Eagle-Picher material, which could trap hydrogen atoms. The second mystery is the larger intensity of the O-H peak as compared to the O-D peak (Fig. 7). The larger intensity may be related to hydrogen's faster diffusion and larger vibrational amplitude, but the size of the difference (x10) is puzzling.

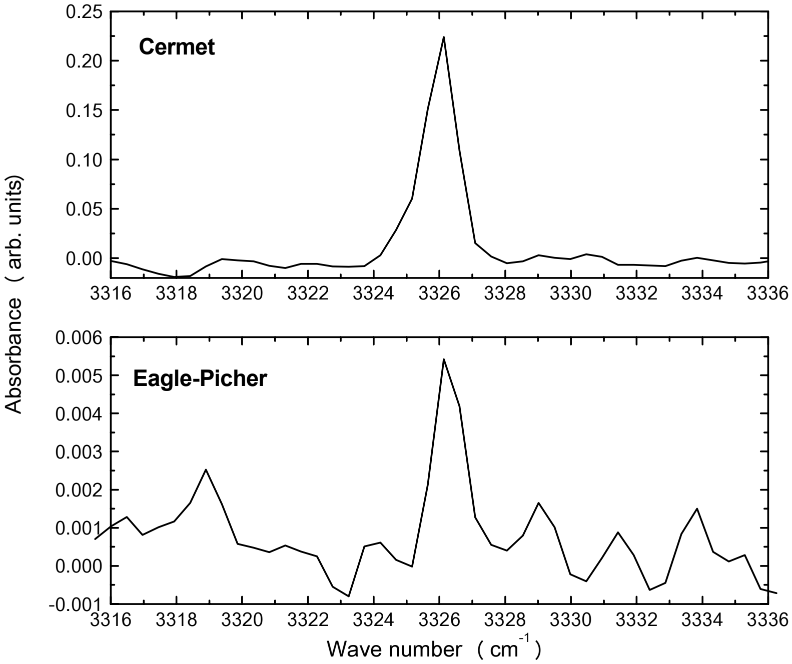

Figure 6. IR spectra of hydrogenated ZnO, at liquid-helium temperatures, for samples purchased from Cermet and Eagle-Picher.

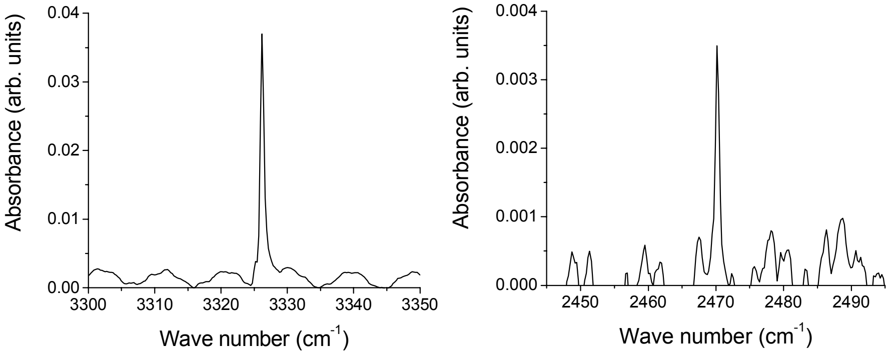

Figure 7. IR spectra of O-H (left) and O-D (right) complexes in ZnO.

5. CONCLUSIONS

Hydrogen donors can be introduced by annealing ZnO in a hydrogen ambient, resulting in O-H complexes. These donor complexes are unstable, however, and decay away in a few months at room temperature. It is likely that most of the O-H complexes form H_2 molecules in the sample. Results of IR spectroscopy are consistent with an O-H complex that is in an antibonding configuration, oriented at some angle to the *c* axis.

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