

Infrared Spectroscopy of Hydrogen in ZnO

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ABSTRACT

Zinc oxide (ZnO) has shown great promise as a wide band gap semiconductor with optical, electronic, and mechanical applications. Recent first-principles calculations and experimental studies have shown that hydrogen acts as a shallow donor in ZnO, in contrast to hydrogen's usual role as a passivating impurity. The structures of such hydrogen complexes, however, have not been determined. To address this question, we performed vibrational spectroscopy on bulk, single-crystal ZnO samples annealed in hydrogen (H₂) or deuterium (D₂) gas. Using infrared (IR) spectroscopy, we have observed O-H and O-D stretch modes at 3326.3 cm⁻¹ and 2470.3 cm⁻¹ respectively, at a sample temperature of 14 K. These frequencies are in good agreement with the theoretical predictions for hydrogen and deuterium in an antibonding configuration, although the bond-centered configuration cannot be ruled out. The IR-active hydrogen complexes are unstable, however, with a dissociation barrier on the order of 1 eV.

INTRODUCTION

Zinc oxide (ZnO) is a wide-bandgap semiconductor that has attracted tremendous interest as a blue light emitting material, a buffer layer for GaN-based devices [1], and a transparent conductor [2]. The stability of excitons in ZnO results in a very high quantum efficiency at temperatures of 300 K and higher, making it an ideal active material for the emission of blue to UV light in high-temperature environments. Theoretical work has predicted ferromagnetism above room temperature for Mn-doped ZnO, an important requirement for spintronic devices [3]. In addition to these device applications, ZnO has a potential application as a scintillator detector, due to the high cross section for nuclear reactions between ⁶⁴Zn and fast neutrons [4].

As-grown ZnO is nearly always *n* type. Recent theoretical work has demonstrated that hydrogen is a shallow donor in ZnO [5], raising the possibility that hydrogen donors may be introduced into the bulk during growth or processing [6,7]. Experimental results on muonium implanted into ZnO [8] and electron-nuclear resonance measurements on lightly doped, *n*-type ZnO [9] have provided evidence that hydrogen is indeed a shallow donor. In order to determine the microscopic structure of hydrogen donors, in previous work, we used infrared (IR) spectroscopy to measure the local vibrational modes (LVMs) arising from these complexes [10]. By comparing with *ab initio* calculations [5], it was proposed that the O-H complex has an antibonding orientation. However, the bond-centered orientation could not be ruled out. Two possible models for the O-H complex are shown in Fig. 1.

We have also performed polarized IR spectroscopy at room temperature [11]. These measurements indicate that the dipole of the O-H complex lies at an angle of approximately 112° to the *c* axis of wurtzite ZnO. No dipoles were observed that were oriented parallel to the *c* axis. Recent work by Nickel *et al.* [12] and Lavrov *et al.* [13] have reported hydrogen-related LVMs that are different from what is reported here.

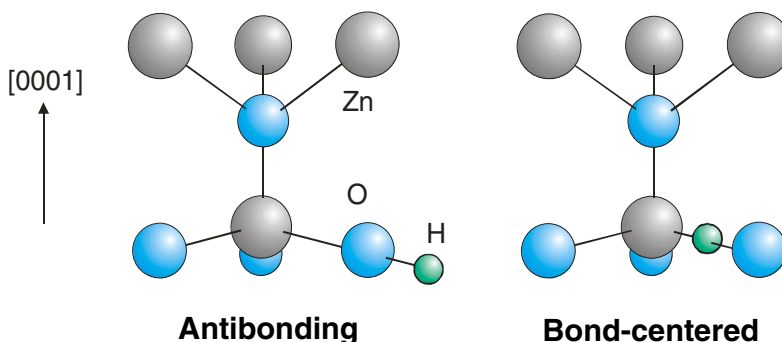


Figure 1. Two possible models for hydrogen donors in ZnO. Theoretically, the O-H complexes may also be aligned along the c axis.

EXPERIMENTAL DETAILS

Bulk, single crystal, c -cut samples of ZnO were obtained from Cermet, Inc [14]. As received, these samples have a free electron concentration of $n \sim 2 \times 10^{17} \text{ cm}^{-3}$. Hydrogen diffusion experiments were performed by sealing a quartz ampoule, evacuated and backfilled with 2/3 atm of hydrogen gas. Along with the sample, the ampoule also contained ZnO powder, in order to minimize damage to the sample surface due to the reduction of ZnO by hydrogen. The ampoule was placed in a horizontal furnace and annealed at a temperature of 720°C for a duration of 10 hr. For the last 10 min of the annealing schedule, the temperature was raised to 850°C. The ampoule was then quenched to room temperature by dropping it into water. The sample was retrieved by breaking the ampoule. After hydrogen diffusion, the free electron concentration increased to $5.5 \times 10^{17} \text{ cm}^{-3}$, consistent with the claim that hydrogen in ZnO is a shallow donor.

Room-temperature Hall-effect measurements (MMR Technologies, Inc.) were performed in the van der Pauw geometry, using a 1 Tesla electromagnet. IR spectroscopy was performed using a Bomem DA8 Fourier transform IR (FTIR) spectrometer and an InSb detector. The O-H LVM was measured at room temperature and low temperatures (~ 14 K). For the low temperature measurements, we used a Janis STVP liquid-helium continuous-flow cryostat with wedged ZnSe windows.

DISCUSSION

Local vibrational modes

Using infrared IR spectroscopy, we have observed O-H and O-D stretch modes at 3326.3 cm^{-1} and 2470.3 cm^{-1} respectively, at a sample temperature of 14 K (Fig. 2). These modes are in agreement with those reported in Ref. 10. We did not observe the O-H modes reported by Lavrov *et al.* [13]. An unusual feature is that the deuterium peak is approximately 10 times weaker than the hydrogen peak, although the annealing conditions were the same. One possible reason for this may be the presence of hydrogen in the as-received samples. Another explanation may be that there is a greater diffusion barrier for deuterium than for hydrogen.

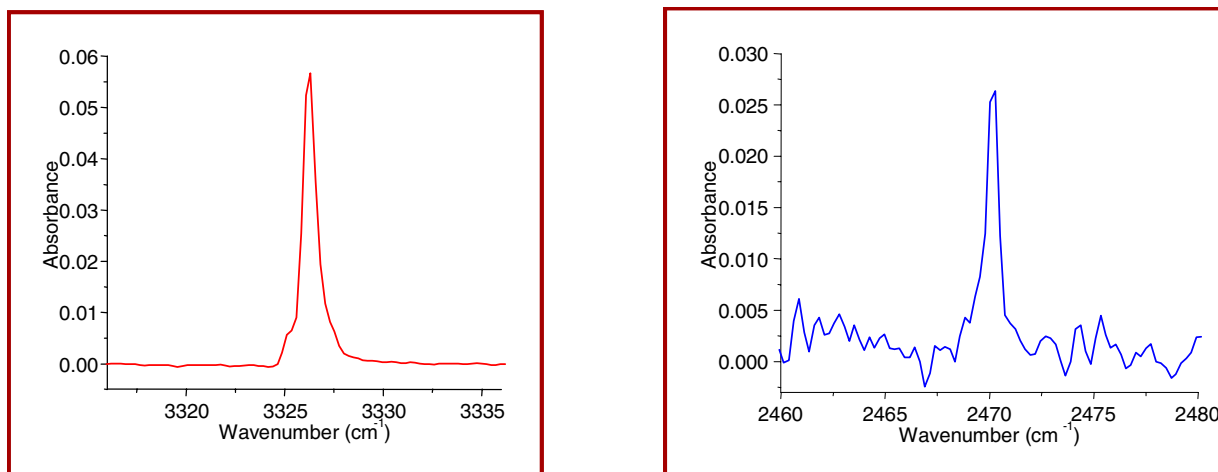


Figure 2. IR absorption spectra of O-H (left) and O-D (right) complexes in ZnO, at a temperature of 14 K.

Instability of O-H complexes

At room temperature, the area of the O-H peak gradually decreases, with a time constant of approximately one month. This behavior indicates that the O-H complexes that we observe are unstable. To investigate the kinetics in more detail, measurements were performed on a sample that had been annealed in a H₂/D₂ gas mixture. This sample contained O-H and O-D peaks. The intensities of these peaks were measured over the course of 50 days. The results are plotted in Fig. 3. The decays are exponential, with time constants of 550 and 814 hr for O-H and O-D complexes, respectively. The slower decay of the O-D complex is consistent with the lower attempt frequency of deuterium as compared to hydrogen.

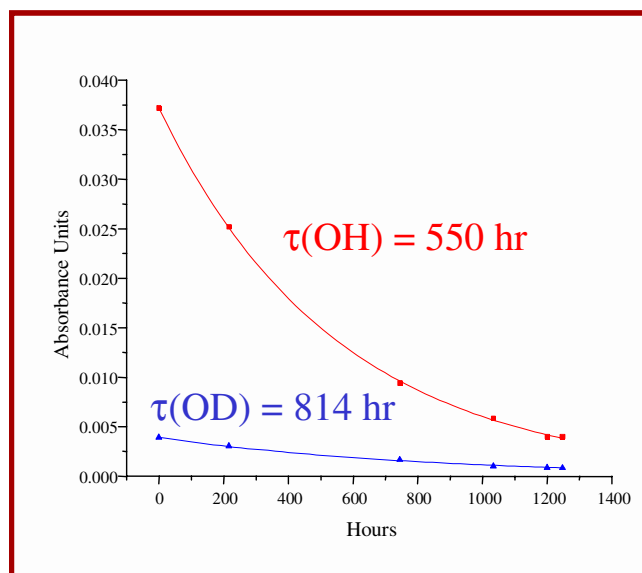


Figure 3. Area of O-H and O-D peaks as a function of time.

Recovery of the O-H complexes

After an O-H absorption peak vanishes, the peak can be recovered by annealing the ZnO sample in open air. To perform this anneal, the ZnO was placed in a quartz tube that was open at one end. The tube was moved into a horizontal furnace that had been pre-heated to 710°C. After approximately 20 s, the quartz tube was removed and dropped into water in order to rapidly quench to room temperature. The ZnO did not come into contact with the water. It should be noted that the sample temperature was not well defined during this annealing treatment. A thermocouple placed in the vicinity of the sample measured the air temperature to be approximately 520°C.

After this open-air anneal, the O-H peak increased from nearly zero to 1/2 to 2/3 its original height. An example is shown in Fig. 4. The recovery of the O-H peak indicates that hydrogen did not leave the sample; rather, hydrogen had gone into an “invisible” complex that is more stable than the O-H complex.

Hall-effect measurements on the sample before the open-air anneal showed a free electron concentration of $n = 2.0 \times 10^{17} \text{ cm}^{-3}$, which is similar to the concentration in as-received samples. After annealing in open air, the concentration increased to $n = 3.0 \times 10^{17} \text{ cm}^{-3}$. These results indicate that the invisible hydrogen complex is electrically neutral. However, more systematic measurements will be required to make that statement definitive. It has been proposed that the invisible hydrogen is in the form of H_2 molecules [15], a hypothesis that is consistent with our observations.

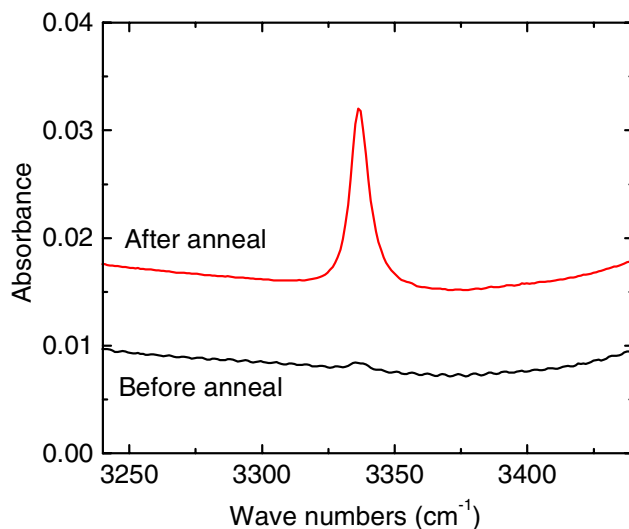


Figure 4. O-H LVM peak before and after annealing in open air. These IR spectra were taken at room temperature.

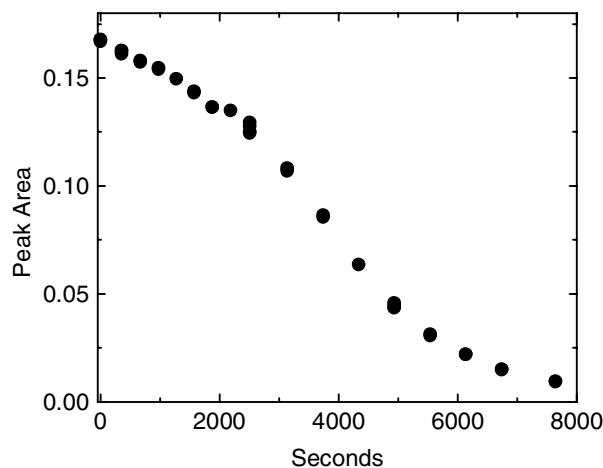


Figure 5. Plot of O-H peak area (measured at room temperature) as a function of annealing time. The annealing temperature was 100°C.

Decay of O-H peak at 100°C

To investigate the kinetics of the O-H decay in more detail, samples were annealed at a temperature of 100°C by boiling in water. Although there exists the possibility of introducing hydrogen from H₂O, the diffusion and solubility is low such that the O-H peak should not be affected by that process.

As shown in Fig. 5, the decay of the O-H complex at 100°C is non-exponential. The reasons for this unusual behavior are not immediately obvious. One possible explanation is that, for early times, there is a source of hidden hydrogen that forms O-H complexes. Eventually, however, the O-H peak decays to zero, as was observed for room-temperature annealing.

CONCLUSIONS

ZnO annealed in hydrogen contains O-H complexes. The O-H and O-D bond-stretching modes were measured by IR spectroscopy. At room temperature, however, these complexes decay over the course of several weeks. The complexes can then be resurrected by rapidly annealing in open air. Preliminary electrical measurements indicate that the “invisible” hydrogen is electrically neutral whereas the IR-active O-H complex is a shallow donor.

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