



# Infrared spectroscopy of hydrogen in annealed zinc oxide

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## Abstract

Zinc oxide (ZnO) has shown great promise as a wide band gap semiconductor with optical, electronic, and mechanical applications. First-principles investigations by C. G. Van de Walle (Phys. Rev. Lett. 85 (2000) 1012) suggest that hydrogen may act as a shallow donor in ZnO. These same predictions also apply to deuterium (D). Using IR spectroscopy we have observed O–H and O–D stretch modes at 3326.3 and 2470.3  $\text{cm}^{-1}$ , respectively, in the same sample at a temperature of 14 K. These frequencies are in good agreement with the theoretical predictions for hydrogen and deuterium in an antibonding configuration. We have also performed preliminary polarization measurements at room temperature showing that the dipole of the O–H complex does not lie parallel to the *c*-axis of wurtzite ZnO.

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In previous studies, it has been shown that hydrogen diffusion [1,2] into zinc oxide (ZnO) will form an O–H complex that is observable via a local vibrational mode (LVM) at 3336.8  $\text{cm}^{-1}$  at room temperature and 3326.2  $\text{cm}^{-1}$  at liquid-helium temperatures [3]. It was also shown that deuterium (D) diffusion into ZnO produces an LVM at 2470  $\text{cm}^{-1}$  at liquid-helium temperatures. These frequencies are both in good agreement with the theoretical prediction for an antibonding configuration [4]. Previous studies have also shown that hydrogen acts as a shallow donor [4–6] and may be an important element in the growth and processing of n-type ZnO. In addition to hydrogen donors, hydrogen-vacancy complexes have been observed with LVM spectroscopy [7].

Mid-infrared (IR) absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform spectrometer (FTIR) with a KBr

beam splitter. The measurements in this study were performed at room temperature (300 K) and near liquid-helium temperatures (14–18 K). For both room temperature and near liquid-helium temperature measurements, an InSb detector was used. Liquid-helium measurements were performed with a Janis STVP continuous flow liquid-helium cryostat with wedged ZnSe windows. The spectral range was 1800–7000  $\text{cm}^{-1}$  and the instrumental resolution was between 0.5 and 2  $\text{cm}^{-1}$ .

Single-crystal ZnO samples were obtained from EaglePicher [8] and Cermet [9]. The average thicknesses for each sample were 0.5 and 1.3 mm, respectively. IR absorption spectra were obtained for as-received ZnO samples prior to our annealing treatments. Unpolarized and polarized IR light traveled along various physical axes of the crystal to search for different dipole orientations of defects and dopants. No evidence of O–H or O–D dipoles was found. The samples were then sealed into individual ampoules with  $\frac{1}{3}$  atm  $\text{H}_2$  and

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$\frac{1}{3}$  atm  $D_2$  along with a ZnO powder paste (allowed to dry under vacuum) made with equal parts  $H_2O$  and  $D_2O$ . Each ampoule was then placed in a horizontal furnace and annealed for 50 h at a temperature of  $710^\circ C$ . After the annealing treatment the sealed ampoule was quenched to room temperature by immersion in water. Almost no degradation was seen in the single-crystal ZnO sample, in contrast to samples that were annealed in  $H_2$  without ZnO powder. This can be attributed to the primary reaction of hydrogen/deuterium with oxygen occurring in the ZnO paste rather than in the single crystal. Once equilibrium was reached, the remaining hydrogen/deuterium gas in the ampoule was sufficient to diffuse into the sample and yield strong LVM absorption peaks.

At room temperature an absorption peak is clearly visible in the samples from Cermet at  $3336.8\text{ cm}^{-1}$  with a width of  $8.7\text{ cm}^{-1}$ , reproducing our previous results [3]. However, the LVM for an O–D complex near  $2470\text{ cm}^{-1}$  was not observed, in part due to high absorbance in that spectral range. This is also in agreement with previous results that showed an extremely weak O–D LVM at liquid-helium temperatures [3]. At liquid-helium temperatures the Cermet sample showed signs of containing both O–H and O–D complexes, observed via the LVM absorption peaks at  $3326.2$  and  $2470.2\text{ cm}^{-1}$  with widths of  $0.74$  and  $0.67\text{ cm}^{-1}$ , respectively (Fig. 1). The peak shift as

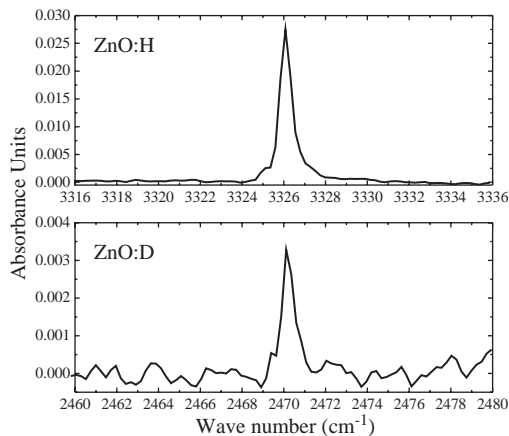


Fig. 1. IR spectra of ZnO annealed in  $H_2$  and  $D_2$ . Top: O–H LVM; bottom: O–D LVM.

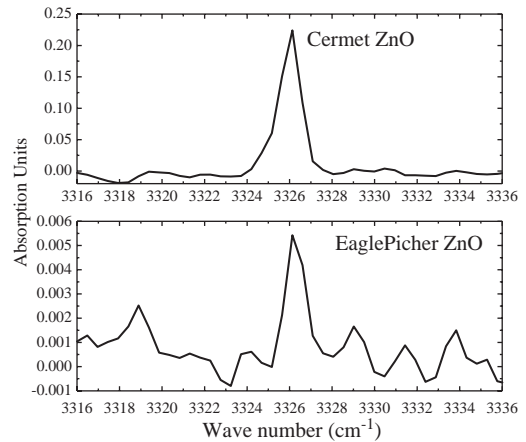


Fig. 2. O–H absorption spectra of Cermet Inc. and EaglePicher ZnO.

well as its narrowing is similar to that of hydrogen LVMs in various semiconductors [10]. However, the O–D peak was significantly weaker than the O–H peak. The reason for this difference is not known.

The O–H peak in the EaglePicher samples was much weaker than that in the Cermet samples (Fig. 2). Nonetheless, it was apparent that the O–D peak was weaker than the O–H peak, consistent with what was observed in the Cermet samples. Due to the stronger LVM absorption peaks and subsequent ease of making observations in the Cermet material, the following experiments were only performed on Cermet material.

Originally, these samples were stored at room temperature. After some time, however, a noticeable decay in the absorption peaks was observed. No other peaks were observed during or after this decay process, making it difficult to determine the final location of the hydrogen or deuterium. After the peaks had nearly disappeared, the sample was reannealed in open air for 5 min at  $710^\circ C$ . This resulted in a resurrection of the peaks to their previous intensities (Fig. 3), an observation that shows that the hydrogen and deuterium did not leave the crystal. In addition, annealing an as-grown sample in open air did not produce these peaks, suggesting that a large concentration of hydrogen was not present in the as-grown samples.

In order to observe this decay properly, the samples were stored in the same location under the

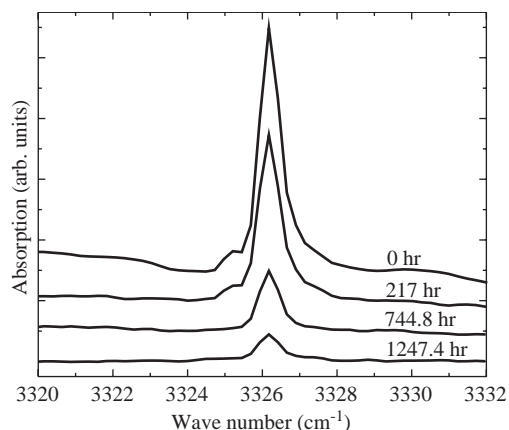


Fig. 3. Decay of the O–H LVM. The annealing temperature was 300 K and the sample temperature was 14 K.

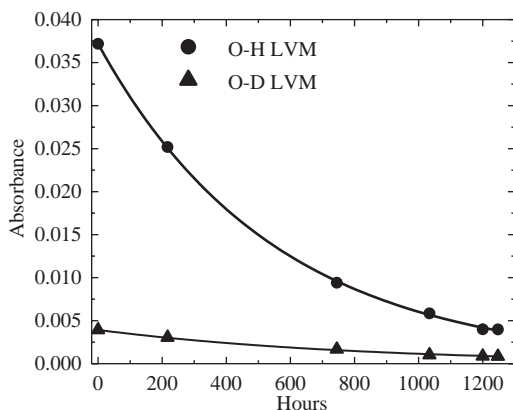


Fig. 4. Decay of the O–H and O–D LVMs. Solid lines are fits to exponential decays.

same conditions while measurements were not being taken. After several measurements over the course of a few months, the decay processes were found to be exponential with decay constants of 550 h for the O–H complex and 814 h for the O–D complex (Fig. 4) as fit by

$$y = A_1 e^{-t/\tau},$$

where  $A_1$  is set to the peak height at  $t = 0$ . These decay constants correspond to half-lives of 381 and 564 h, respectively. Previous observations show that the decay does approach zero. It is expected that temperatures between room temperature and the original annealing temperature

will yield different minima, as each temperature will set a new equilibrium. The kinetic equation

$$\frac{1}{\tau} = \nu e^{-E/kT},$$

where  $\tau$  is the decay constant calculated earlier,  $\nu$  is the attempt frequency (assumed to equal the LVM frequency), and  $T$  is the annealing temperature (300 K), was used to give a preliminary calculation for the barrier height. The derived energy barriers are approximately 1.2 eV for both O–H and O–D complexes. Future studies, which vary  $T$ , will be performed to find these energy values more accurately.

In order to determine the orientation of the O–H complex, a polarizer was placed between the sample and the incident IR beam. Samples with the  $c$ -axis perpendicular to the sample surface were sliced to perform this measurement. The maximum peak intensity was observed for polarization perpendicular to the  $c$ -axis. As the polarization of the incident light approached parallel to the  $c$ -axis, the absorption peak at  $3336.8 \text{ cm}^{-1}$  decreased to 0.33 that of the perpendicular orientation (Fig. 5). Using this ratio, the angle between the O–H dipoles and the  $c$ -axis ( $\theta$ ) was determined by the equation

$$\frac{I_{P\parallel c}}{I_{P\perp c}} = \frac{3 \cos^2 \theta}{\frac{3}{2} \sin^2 \theta} = 2 \cot^2 \theta,$$

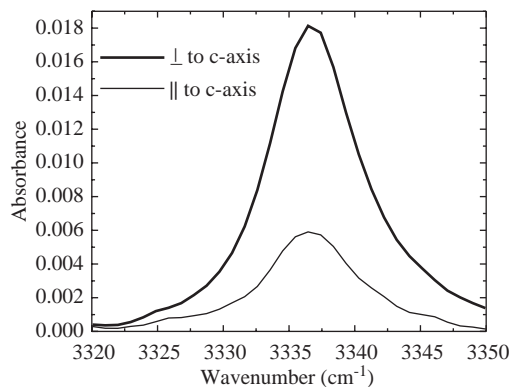


Fig. 5. Polarized IR spectra of the O–H complex at room temperature in sample with  $c$ -axis parallel to sample surface. The reduction in intensity shows that the O–H dipole does not lie parallel to the  $c$ -axis.

where  $I_{P\parallel c}$  and  $I_{P\perp c}$  are the peak intensities for polarizations parallel and perpendicular to the  $c$ -axis, respectively. A solution to this equation is  $\theta = 112.1^\circ$ , in good agreement with the tetrahedral angle of  $\theta = 109^\circ$ . There were no noticeable changes in peak intensity for different polarizations when the propagation vector was parallel to the  $c$ -axis.

In conclusion, the location of hydrogen shortly after annealing the samples is in a configuration with oxygen oriented  $112.1^\circ$  from the  $c$ -axis. This position is unstable, however, and decays fairly slowly at room temperature. The final location of the hydrogen cannot be determined, as of yet, by these results. Future research will determine the energy potential in which the unstable O–H complex lies. This will provide a better understanding of the structure of the O–H complex and where the hydrogen relocates after time. It is also noted that hydrogen in ZnO from EaglePicher may have a different site preference than in ZnO from Cermet, resulting in a weaker O–H peak. One possibility is that EaglePicher samples contain more oxygen vacancies, which trap hydrogen atoms. Future studies involving positron annihilation spectrometry will be performed to address this issue.

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## References

- [1] E. Mollwo, *Z. Phys.* 138 (1954) 478.
- [2] D.G. Thomas, J.J. Lander, *J. Chem. Phys.* 25 (1956) 1136.
- [3] M.D. McCluskey, S.J. Jokela, K.K. Zhuravlev, P.J. Simpson, K.G. Lynn, *Appl. Phys. Lett.* 81 (2002) 3807.
- [4] C.G. Van de Walle, *Phys. Rev. Lett.* 85 (2000) 1012.
- [5] S.F.J. Cox, E.A. Davis, S.P. Cottrell, P.J.C. King, J.S. Lord, J.M. Gil, H.V. Alberto, R.C. Vilão, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R.L. Lichti, S.J.C. Irvine, *Phys. Rev. Lett.* 86 (2001) 2601.
- [6] D.M. Hoffman, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, P.G. Baranov, *Phys. Rev. Lett.* 88 (2002) 045504.
- [7] E.V. Lavrov, J. Weber, F. Börrnert, C.G. Van de Walle, R. Helbig, *Phys. Rev. B* 66 (2002) 165205.
- [8] EaglePicher, [www.epcorp.com](http://www.epcorp.com).
- [9] Cermet Inc., [www.cermetinc.com](http://www.cermetinc.com).
- [10] M.D. McCluskey, E.E. Haller, in: *Semiconductors and Semimetals*, Vol. 61, Academic, New York, 1999 (Chapter 9).