

Infrared spectroscopy of hydrogen in ZnO

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Zinc oxide (ZnO) is a wide-band gap semiconductor that has attracted tremendous interest for optical, electronic, and mechanical applications. First-principles calculations by [C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000)] have predicted that hydrogen impurities in ZnO are shallow donors. In order to determine the microscopic structure of hydrogen donors, we have used IR spectroscopy to measure local vibrational modes in ZnO annealed in hydrogen gas. An oxygen–hydrogen stretch mode is observed at 3326.3 cm^{-1} at a temperature of 8 K, in good agreement with the theoretical predictions for hydrogen in an antibonding configuration. The results of this study suggest that hydrogen annealing may be a practical method for controlled *n*-type doping of ZnO.

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Zinc oxide (ZnO) is a wide-band gap semiconductor that has attracted tremendous interest as a blue light emitting material,¹ a substrate for GaN-based devices,² and a transparent conductor³ in solar cells.^{4,5} ZnO has large piezoelectric constants,⁶ making it a useful transducer material⁷ for applications in microelectrical-mechanical systems. As grown, ZnO is almost always *n* type. While many researchers have attributed the *n*-type conductivity to native defects, recent theoretical work has demonstrated that hydrogen is a shallow donor in ZnO⁸ that may be introduced into the bulk during growth or processing.⁹ Experimental results on muonium in ZnO¹⁰ and electron nuclear double resonance measurements on nominally undoped ZnO¹¹ have supported the claim that hydrogen is a shallow donor. In order to determine the microscopic structure of hydrogen donors, we have used IR spectroscopy to measure the local vibrational modes (LVMs) arising from these complexes. By comparing with *ab initio* calculations,⁸ we can propose a model for O–H complexes in ZnO.

Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform spectrometer with a KBr beamsplitter. Samples were measured at room temperature (300 K) and liquid-helium temperatures (7–9 K). For the room temperature measurements, a mercury–cadmium–telluride detector was used. For the liquid helium measurements, the samples were placed in a Janis STVP continuous-flow liquid-helium cryostat with wedged ZnSe windows, and an InSb detector¹² was used. The spectral range was $500\text{--}5000\text{ cm}^{-1}$ and the instrumental resolution was $0.5\text{--}2\text{ cm}^{-1}$. Spectra were taken at several different resolutions to ensure

that instrumental broadening did not affect the measured peak widths.

IR absorption spectra were obtained for an undoped, single-crystal ZnO sample. The sample was cut into a cylindrical shape, with a diameter of 9.7 mm and a length of 6.0 mm. Unpolarized IR light traveled along the length (*c* axis) of the cylinder. Spectra were taken of this sample at room temperature (Fig. 1). The sample was then sealed in a quartz ampoule with $\frac{1}{2}$ atm H₂ gas. The ampoule was placed in a horizontal furnace and annealed at a temperature of 700 °C for a duration of 120 h. According to the experimental work

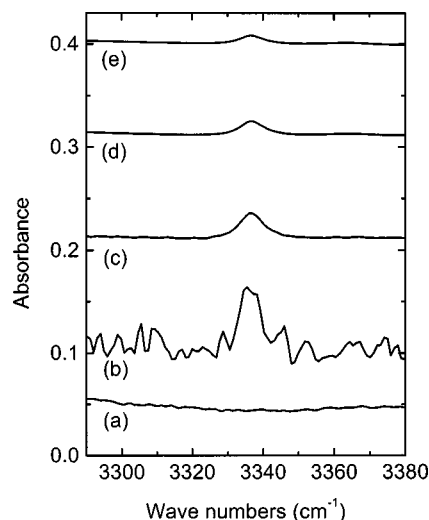


FIG. 1. Room-temperature IR absorption spectra of a 6-mm-thick ZnO sample (a) as grown and (b) after annealing in hydrogen gas. The annealed sample was then polished to thicknesses of (c) 4.3, (d) 3.0, and (e) 1.7 mm. Spectra are offset vertically for clarity.

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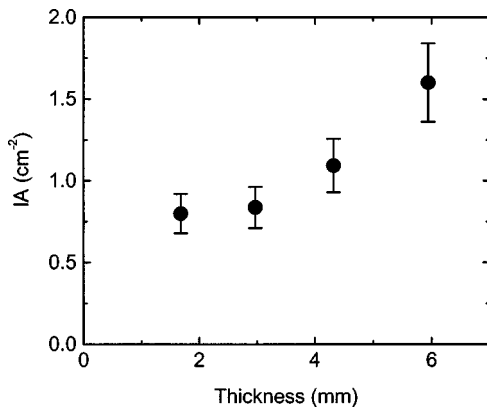


FIG. 2. IA of the O–H LVM in ZnO, as a function of sample thickness.

of Thomas and Lander,⁹ these annealing conditions should result in a diffusion length of 6 mm, which is enough for hydrogen to diffuse through the bulk of our sample. Following the annealing treatment, the ampoule was quenched to room temperature by immersion in water. The sample showed some decomposition in the form of pits on the surface, presumably due to reduction of ZnO by hydrogen. In spite of the surface damage, the transmitted IR intensity was sufficient for the measurements in this study.

IR spectra of ZnO annealed in hydrogen are shown in Fig. 1. At room temperature, an IR absorption peak is observed at 3336.8 cm^{-1} , with a full width at half maximum (FWHM) of 8 cm^{-1} . The relatively high noise level in the spectrum for the 6-mm-thick annealed sample [Fig. 1(b)] is consistent with strong free-carrier absorption, which would be expected if hydrogen is a donor impurity. The observed frequency of 3336.8 cm^{-1} is similar to the LVM frequencies arising from O–H complexes in GaAs, which have a stretch-mode frequency of 3300 cm^{-1} at liquid-helium temperatures.¹³ Hence, it is reasonable to assign our IR absorption peak to the stretch mode of O–H complexes in ZnO.

In order to reduce the free-carrier background and the surface damage, the sample was successively polished to thicknesses of 4.3, 3.0, and 1.7 mm. After each polishing step, room-temperature IR spectra were obtained. As shown in Fig. 1, the intensity of the IR absorption peak decreased as the sample thickness was reduced. The integrated absorbance (IA) is defined as

$$IA = \int \alpha(\nu) d\nu, \quad (1)$$

where $\alpha(\nu)$ is the absorption coefficient (cm^{-1}) and ν is the LVM frequency in wave numbers (cm^{-1}). The IA for the O–H LVM, at room temperature, is plotted in Fig. 2. The decrease in IA as the sample is thinned indicates that the hydrogen concentration near the surface is slightly greater than that in the bulk.

According to Thomas and Lander,⁹ the solubility of hydrogen for our annealing conditions is $4 \times 10^{17}\text{ atoms/cm}^3$. If all the hydrogen atoms formed O–H complexes, then our results yield an integrated absorbance given by $IA\text{ (cm}^2) \sim 2 \times 10^{-18} N\text{ (cm}^{-3})$, where N is the concentration of O–H complexes. However, some hydrogen atoms may be present in other configurations, such as H_2 molecules or hydrogen-

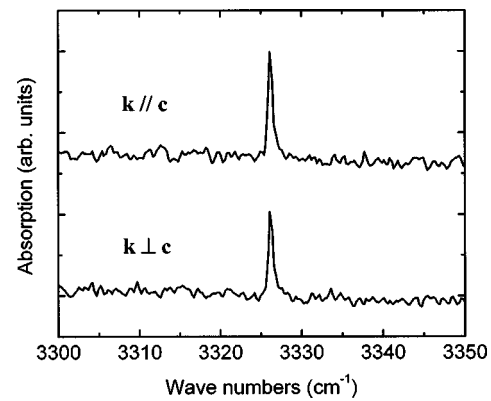


FIG. 3. IR absorption spectra of the O–H LVM in ZnO at a temperature of 8 K. The propagation of IR light was parallel to the c axis ($\mathbf{k}\parallel\mathbf{c}$) and perpendicular to the c axis ($\mathbf{k}\perp\mathbf{c}$). Spectra are offset vertically for clarity.

decorated oxygen vacancies. Therefore, our estimate for the coefficient (2×10^{-18}) should be regarded as a lower bound.

For the 1.7-mm-thick sample, the O–H LVM was observed at liquid-helium temperatures (Fig. 3). At a temperature of 8 K, the peak has a frequency of 3326.3 cm^{-1} and a FWHM of 0.7 cm^{-1} . The shift in frequency and narrowing of the linewidth upon cooling to liquid-helium temperatures are consistent with the observed behavior of hydrogen LVMs in numerous compound semiconductors.¹⁴ Two sample geometries were used, in which light propagated parallel to the c axis ($\mathbf{k}\parallel\mathbf{c}$) and perpendicular to the c axis ($\mathbf{k}\perp\mathbf{c}$). No new peaks were observed for $\mathbf{k}\perp\mathbf{c}$, suggesting that there are no complexes with dipoles aligned along the c axis. The ratio of the peak intensities is $I(\mathbf{k}\perp\mathbf{c})/I(\mathbf{k}\parallel\mathbf{c})=0.8$. If one assumes that all the dipoles are oriented with an angle θ to the c axis, then the classical intensity ratio is given by

$$I(\mathbf{k}\perp\mathbf{c})/I(\mathbf{k}\parallel\mathbf{c}) = 1/2 + \cot^2 \theta. \quad (2)$$

From Eq. (2), we derive $\theta=119^\circ$, which is slightly larger than the tetrahedral angle $\theta=109^\circ$. Given the uncertainties in the measurement, and the fact that the light is not perfectly collimated, our results are consistent with the tetrahedral angle.

The LVM frequency of 3326.3 cm^{-1} is consistent with the first-principles calculations of Van de Walle.⁸ In that work, the calculated O–H stretch-mode frequencies were 3680 and 3550 cm^{-1} for the bond-centered and antibonding configurations, respectively, in the harmonic approximation. In order to estimate the effect of anharmonicity, we note that for diatomic OH molecules in the gas phase, the anharmonic terms in the potential cause the stretch-mode frequency to shift downward by 166 cm^{-1} .¹⁵ Subtracting that shift from the calculated frequency for the antibonding O–H complex yields a frequency of 3384 cm^{-1} , in reasonable agreement with our observation (3326.3 cm^{-1}). The actual anharmonicity may be different from our estimate, however, so the bond-centered configuration cannot be ruled out.

To further investigate the IR spectrum of hydrogen in ZnO, a thin (0.5 mm) sample was annealed in deuterium gas at a temperature of 700°C for 2 h. The low thickness of the sample allowed us to measure the free-carrier absorption over a large wavelength range. The room-temperature IR absorption spectrum of the annealed sample is shown in Fig. 4. The spectrum of an as-grown sample was used as the refer-

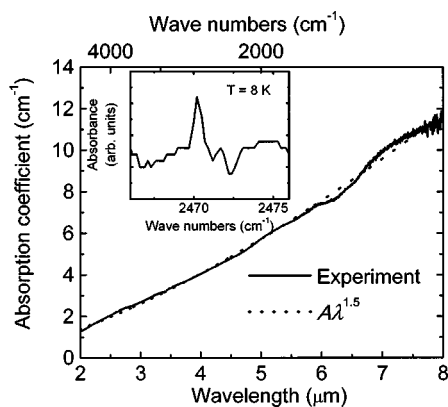


FIG. 4. Room-temperature free-carrier absorption of ZnO annealed in deuterium gas. An IR absorption peak attributed to O–D complexes is shown in the inset.

ence. The increased absorption due to annealing is consistent with free-carrier absorption from deuterium donors. The absorption coefficient was modeled by $\sigma = A\lambda^p$, where A and p are adjustable parameters. A least-squares fit yields $p = 1.5$, which is expected for free-carrier absorption from electrons that are scattered by acoustic phonons.¹⁶ At a temperature of 8 K, the IR spectrum of ZnO annealed in deuterium showed a weak peak at 2470.3 cm^{-1} (Fig. 4, inset), which we tentatively attribute to O–D complexes. The isotopic frequency ratio between the O–H and O–D modes is $r = 1.3465$, in excellent agreement with the value for O–H complexes in GaP ($r = 1.3464$).¹⁷

In conclusion, we have observed an IR absorption peak arising from O–H complexes in ZnO after annealing in hydrogen gas. The observed LVM frequency is in good agreement with the predictions of first-principles calculations. Our observations are consistent with hydrogen in an antibonding configuration, oriented at an angle of $\sim 110^\circ$ to the c axis.

The results of this study suggest that hydrogen annealing may be a practical method for controlled n -type doping of ZnO.

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¹D. C. Look, *Mater. Sci. Eng.*, B **80**, 383 (2001).

²J. E. Nause, III-*Vs Review* **12**, 28 (1999).

³T. Minami, *MRS Bull.* **25**, 38 (2000).

⁴A. Nuruddin and J. R. Abelson, *Thin Solid Films* **394**, 49 (2001).

⁵J. C. Lee, K. H. Kang, S. K. Kim, K. H. Yoon, I. J. Park, and J. Song, *Sol. Energy Mater.* **64**, 185 (2000).

⁶Y. Noel, C. M. Zicovich-Wilson, B. Civalleri, P. D'Arco, and R. Dovesi, *Phys. Rev. B* **65**, 014111 (2002).

⁷P. M. Martin, M. S. Good, J. W. Johnston, G. J. Posakony, L. J. Bond, and S. L. Crawford, *Thin Solid Films* **379**, 253 (2000).

⁸C. G. Van de Walle, *Phys. Rev. Lett.* **85**, 1012 (2000).

⁹D. G. Thomas and J. J. Lander, *J. Chem. Phys.* **25**, 1136 (1956).

¹⁰S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Viao, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, *Phys. Rev. Lett.* **86**, 2601 (2001).

¹¹D. M. Hoffman, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt, and P. G. Baranov, *Phys. Rev. Lett.* **88**, 045504 (2002).

¹²InfraRed Associates, Inc. (www.irassociates.com).

¹³B. Pajot and C. Song, *Phys. Rev. B* **45**, 6484 (1992).

¹⁴M. D. McCluskey and E. E. Haller, in *Semiconductors and Semimetals* (Academic, New York, 1999), Vol. 61, Chap. 9.

¹⁵G. Herzberg, *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules* (Krieger, Malabar, FL, 1989), p. 560.

¹⁶J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 74–75.

¹⁷W. Ulrici, M. Czupalla, and M. Seifert, *Phys. Status Solidi B* **210**, 551 (1998).