Structure and stability of O-H donors in ZnO from high-pressure and infrared spectroscopy

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Zinc oxide (ZnO) is a wide-band-gap semiconductor with potential optical, electronic, and mechanical applications. First-principles investigations [C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000)] predicted that hydrogen impurities act as shallow donors in ZnO. IR spectroscopy [M. D. McCluskey *et al.*, Appl. Phys. Lett. **81**, 3807 (2002)] showed that a local vibrational mode at 3326.3 cm^{-1}, at liquid-helium temperatures, corresponded to an O-H type bond. The microscopic structure of this hydrogen complex, however, was not determined. In this Brief Report, the structure and stability of O-H complexes are discussed. The second excited state of the O-H stretch mode was found at 6389 cm^{-1}, allowing us to compare the experimental results with the harmonic calculations of Van de Walle. Results from high-pressure and polarized IR spectroscopy strongly suggest that hydrogen occupies an antibonding location with an O-H bond oriented at an angle of 111° to the *c* axis. By correlating the IR absorbance strength with free-electron concentration, it was established that the O-H complexes are shallow donors. However, the O-H donors are unstable, decaying significantly after several weeks at room temperature. The kinetics of the dissociation follow a bimolecular decay model, consistent with the formation of H_2 molecules.

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Zinc oxide (ZnO), a wide-band-gap semiconductor, has attracted renewed interest with potential applications as a blue light emitting material,[1] a buffer layer for GaN-based devices,[2] a transparent conductor in solar cells,[3,4] a transparent transistor,[5] and as a transducer[6] for microelectrical-mechanical systems. Nearly a half century after the experimental work of Mollwo[7] and Thomas and Lander,[8] first-principles calculations by Van de Walle[9] showed that hydrogen could be a shallow donor in ZnO, raising the possibility that hydrogen donors may be an important source of *n*-type conductivity in this material. Motivated by the theoretical predictions, experiments on muonium implanted into ZnO[10] and electron-nuclear resonance measurements on *n*-type ZnO[11] supported the hypothesis that hydrogen is a shallow donor. Several other studies[12–14] show evidence that hydrogen is related to *n*-type conductivity in ZnO. A study by Shi *et al.*[15] has also shown that hydrogen is sometimes present in as-grown ZnO and is partially responsible for its *n*-type conductivity.

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.[16,17] Although it was established conclusively that hydrogen forms O-H complexes, the microscopic structure of these complexes was not determined. Two possible models for the O-H complex are shown in Fig. 1: the antibonding ($AB_{O,\perp}$) and bond-centered ($BC_{\perp}$) configurations. In both of these models, the O-H bond is oriented at a nearly tetrahedral angle with respect to the *c* axis. Theoretical studies also proposed $AB_{O,\parallel}$ and $BC_{\parallel}$ configurations, where the O-H bond is parallel to the *c* axis. Since the predicted LVM frequencies for all these models are similar, further experiments were required to identify the correct one.

In the present work, IR spectra were obtained using a Bomem DA8 vacuum Fourier transform infrared spectrometer. Low-temperature measurements were obtained using a Janis STVP continuous-flow liquid-helium cryostat with wedged ZnSe windows. Elevated temperature measurements were obtained using a resistive carbon block heater designed to allow for simultaneous heating and IR spectroscopy. The temperature of the sample was measured by a type-K thermocouple. As an additional check, the temperature was also inferred from the frequency shift of the O-H peak. Carrier densities were obtained using Hall-effect measurements in the Van der Pauw geometry. Hydrostatic pressure was applied to the sample using a diamond anvil cell (DAC) with liquid nitrogen as an ambient fluid. *In situ* pressure calibration was obtained within the DAC by measuring IR vibrational modes of CO_2 impurities.[18]
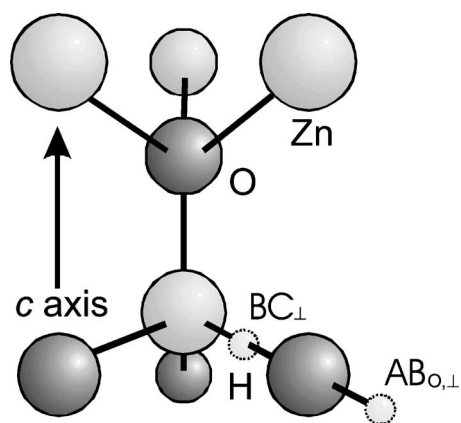

FIG. 1. Two different locations for hydrogen in ZnO. Relaxation of the atoms is not shown.
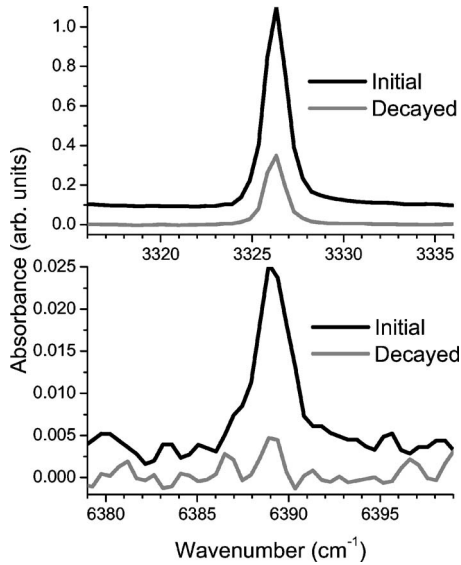
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FIG. 2. IR absorbance due to the first (3326.3 cm^{-1}) and second (6389.1 cm^{-1}) excited state of the O‑H bond-stretching mode in ZnO. A subsequent measurement, shown in gray, reveals that both peaks have decayed. Spectra have been offset for clarity.

ZnO:H samples were prepared using bulk single crystals from Cermet, Inc.[19] The samples were sealed in a quartz ampoule with $\frac{2}{3}$ atm. H_2 gas. The sealed ampoule was then placed into a horizontal furnace at a temperature of 710 °C and treated for a minimum of 10 h followed by a rapid quench to room temperature.

IR measurements at liquid-helium temperatures have revealed a weak absorption peak located at 6389.1 cm^{-1}, with a height approximately 1/50th that of the peak at 3326.3 cm^{-1} (Fig. 2). After two months, both peaks decayed significantly. The peaks at 3326.3 and 6389.1 cm^{-1} are attributed to the first and second excited state, respectively, of the O‑H bond-stretching mode. The frequency of the second excited state allows us to compare our results with the harmonic approximation used by Van de Walle.[9] Using the Morse potential[20,21] as a model, the energy eigenstates are given by

$$E_n = \omega_e \left(n + \tfrac{1}{2} \right) \left[1 - x_e \left(n + \tfrac{1}{2} \right) \right], \tag{1}$$

where x_e accounts for the anharmonicity of the potential. Equation (1) is used to calculate the energy levels E_0, E_1, and E_2. The first and second excited states are given by

$$\Delta E_1 = E_1 - E_0 = \omega_e - 2\omega_e x_e \tag{2}$$

and

$$\Delta E_2 = E_2 - E_0 = 2\omega_e - 6\omega_e x_e, \tag{3}$$

respectively. The harmonic frequency is given by ω_e and the anharmonic term is $\omega_e x_e$. Using 3326 cm^{-1} and 6389 cm^{-1} for the energies of the first and second excited states, we find that $\omega_e = 3589$ cm^{-1}, in good agreement with the calculated harmonic frequency of 3550 cm^{-1} for hydrogen in an AB location.[9] The anharmonic shift is given by $2\omega_e x_e = -263$ cm^{-1}.
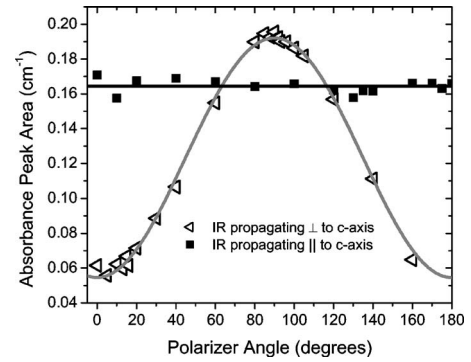

FIG. 3. Polarized IR spectra of the 3336.7 cm^{-1} absorbance peak in ZnO:H at room temperature. For IR light propagating $\perp$ to the c axis, 0° corresponds to polarization $\parallel$ to the c axis. The gray line is a $\sin^2 \theta$ fit.

Polarized IR spectroscopy was used to determine the angle of the O‑H bond with respect to the c axis. Figure 3 shows the O‑H absorbance peak area as a function of polarizer angle for c-cut and a-cut ZnO, with IR transmission at normal incidence. The data for the c-cut crystal show that there is no angular dependence for the O‑H absorbance, indicating that the O‑H bonds are oriented symmetrically around the c axis. For the a-cut crystal, the maximum intensity was observed for a polarization angle perpendicular to the c axis. The angle θ that the O‑H dipoles make with the c axis can be estimated by

$$\frac{I_{P\parallel c}}{I_{P\perp c}} = \frac{3 \cos^2 \theta}{\tfrac{3}{2} \sin^2 \theta} = 2 \cot^2 \theta, \tag{4}$$

where $I_{P\parallel c}$ and $I_{P\perp c}$ are the absorbance peak areas for polarization parallel and perpendicular to the c axis, respectively. The ratio obtained from the fit to the data in Fig. 3 is 0.284, which yields $\theta = 110.6°$, in excellent agreement with a tetrahedral bond angle. This shows that hydrogen lies along a tetrahedral Zn-O bond either in a BC$_\perp$ or AB$_{O,\perp}$ configuration.

To further probe the structure of O‑H donors, the LVM was measured as a function of hydrostatic pressure. According to first-principles calculations by Limpijumnong and Zhang,[22] 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. Figure 4 shows how the O‑H vibrational mode at 3326.3 cm^{-1} (as measured at liquid helium temperatures) shifts towards lower wavenumber with increasing pressure, in qualitative agreement with the AB$_{O,\perp}$ model. A least-square fit yields

$$\upsilon(\text{cm}^{-1}) = 3326.4 - 1.84P + 0.069P^2, \tag{5}$$

where P is the pressure in GPa. The magnitude of the slope (1.8 cm^{-1}/GPa) is lower than the calculated value (4 cm^{-1}/GPa).[22] The slight decrease in the magnitude of the slope is consistent with results from hydrogen in other semiconductors. In all reported cases, the magnitude of the pressure-induced frequency shift is sublinear for AB configurations[23] and supralinear for BC configurations.[24]

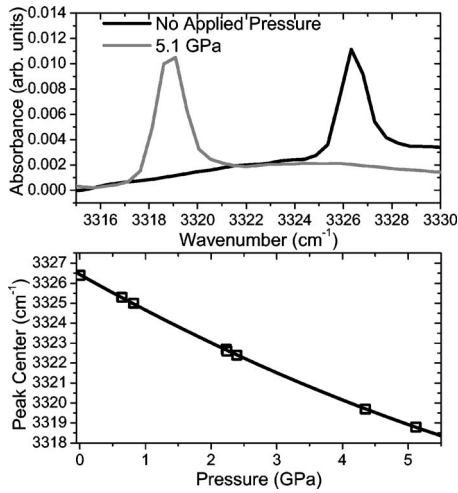Van de Walle calculated formation energies for hydrogen

FIG. 4. Pressure dependence of the O-H bond-stretching frequency. The solid line is a polynomial least-squares fit [Eq. (5)]. Spectra were taken at liquid-helium temperatures with a resolution of 1.0 cm^{-1}.

in several different configurations within ZnO.[9] While hydrogen in the $BC_\perp$ and $BC_\parallel$ configurations have the lowest formation energies (−1.84 eV and −1.82 eV, respectively), they also have the largest net displacement for the neighboring Zn and O atoms. It is possible that the large relaxation presents a significant barrier to the formation of BC complexes.[25] The $AB_{O,\perp}$ and the $AB_{O,\parallel}$ configurations have formation energies of −1.78 eV and −1.59 eV, respectively. The prediction that $AB_{O,\perp}$ has a lower energy than $AB_{O,\parallel}$ is in agreement with our polarized IR results.

The second part of this study deals with the stability of hydrogen in the $AB_{O,\perp}$ location. These O-H bonds decay over time at room temperature, perhaps forming H_2 molecules, which would be nearly invisible to IR spectroscopy.[15] Such a decay is described by a bimolecular model, in which hydrogen atoms combine to form H_2:

$$y(t) = \frac{y_0}{y_0 kt + 1} + y_{t\to\infty}. \tag{6}$$

In this equation, y_0 represents the initial O-H concentration, k is the decay constant, and $y_{t\to\infty}$ represents the minimum value that y approaches as t increases.[26] Equation (6) describes the observed decay better than a standard exponential decay, although it deviates from the data for slightly longer times (Fig. 5).

The formation and decay of O-H complexes is well correlated with the free-electron concentration. The as-received ZnO sample had an electron carrier density of 1.8×10^{17} cm^{-3}. Immediately after hydrogen annealing, the electron carrier density increased to 4.3×10^{17} cm^{-3}. The carrier density and the O-H IR absorbance peak were monitored separately for two ZnO:H samples that had been simultaneously hydrogenated in the same ampoule. The results in Fig. 5 show that the two decaying values are very well correlated, providing conclusive evidence that the O-H complexes are shallow donors. From Fig. 5 we can deduce a calibration factor (ξ) for the following equation:
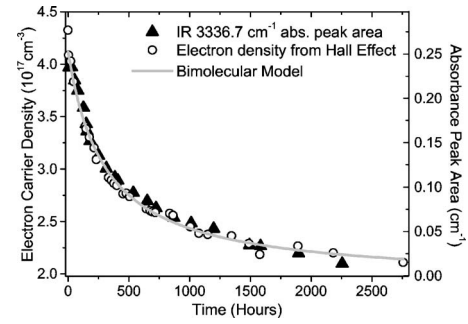

FIG. 5. Plot of the O-H IR absorbance peak area and the carrier concentration at room temperature. Both quantities decay following a bimolecular model (gray line).

$$N = \xi \int \alpha(\nu)d\nu, \tag{7}$$

where N is the O-H donor concentration (cm^{-3}) and the integral is the area of the absorption coefficient for the O-H absorbance peak (cm^{-2}). The absorption coefficient is

$$\alpha(\nu) = \frac{A(\nu)}{x} \ln(10), \tag{8}$$

where $A(\nu)$ is the absorbance, x is the sample thickness, and ν is frequency (cm^{-1}). Figure 5 shows the absorbance peak area and the free-electron concentration as a function of time, from which an average calibration factor of $\xi = 1.6 \times 10^{16}$ cm^{-1} is obtained. This value is in good agreement with hydrogen-related complexes in other semiconductors.[27]

At longer times, the IR absorbance peak decays more rapidly than the electron concentration, suggesting the formation of a "hidden" hydrogen donor. Such a hydrogen donor would explain why the electron carrier density approaches 2.0×10^{17} cm^{-3} rather than its initial value of 1.8×10^{17} cm^{-3}. Evidence of this "hidden" hydrogen donor has also been observed in as-grown ZnO.[15] One candidate for the hidden donor is a hydrogen-decorated oxygen vacancy, which may have an LVM frequency below our measurement range.[28]
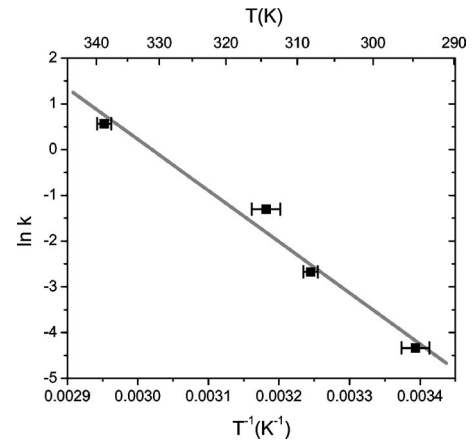

FIG. 6. Plot of ln(k) as a function of inverse temperature, yielding an activation energy (E_a) of 0.96 eV.

The decay of the O-H peak was measured at several different temperatures. Figure 6 shows the plot of the log of the decay constant as a function of inverse temperature. The data were fit by

$$\ln k = A - \frac{E_a}{k_B T}, \tag{9}$$

yielding an activation energy $E_a = 0.96$ eV. This value agrees with the diffusion activation energy measured by Mollwo (1.12 eV) and Thomas and Lander (0.91 eV), suggesting that the formation of H_2 molecules in this temperature range is diffusion-limited.

In conclusion, polarized IR measurements showed that the O-H bond lies 110.6° from the c axis of ZnO:H, in agreement with the $AB_{O,\perp}$ and $BC_\perp$ models. High pressure studies show a decrease in frequency with applied pressure. By comparing with first-principles investigations, we conclude that the $AB_{O,\perp}$ model is the most likely configuration. While hydrogen in the $AB_{O,\perp}$ configuration acts as a donor, it is not stable. The decay is explained by a bimolecular model, consistent with the formation of neutral H_2 molecules within the ZnO crystal.

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