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Unambiguous identification of nitrogen-hydrogen complexes in ZnO

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Zinc oxide (ZnO) is a wide-band-gap semiconductor with a range of potential applications in optoelectronics. The lack of reliable *p*-type doping, however, has prevented it from competing with other semiconductors such as GaN. In this Brief Report, we report the successful incorporation of nitrogen-hydrogen (N-H) complexes in ZnO during chemical vapor transport growth, using ammonia as an ambient. The N-H bond-stretching mode gives rise to an infrared absorption peak at 3150.6 cm^{-1}. Substitutions of deuterium for hydrogen and ^{15}N for ^{14}N result in the expected frequency shifts, thereby providing an unambiguous identification of these complexes. The N-H complexes are stable up to ~700 °C. The introduction of neutral N-H complexes could prove useful in achieving reliable *p*-type conductivity in ZnO.

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Zinc oxide (ZnO) is a semiconductor that has attracted resurgent interest as an electronic material for a range of applications.[1] A wide-band-gap semiconductor, ZnO emits light in the blue-to-UV region of the spectrum with an efficiency that is higher than more conventional materials such as GaN,[2] making ZnO a strong candidate for energy-efficient white lighting. Another major advantage of ZnO is the fact that, in contrast to GaN, large single crystals can be grown relatively inexpensively.[3] ZnO has already been used as a transparent conductor[4] in solar cells[5] and is a preferred material in transparent transistors, "invisible" devices which could be incorporated into products such as liquid-crystal displays.[6]

Despite its desirable properties and potential applications, the lack of reliable *p*-type doping has prevented ZnO from becoming a leader in optoelectronic applications. According to first-principles calculations, substitutional nitrogen (N_O) is an acceptor with a hole binding energy of 400 meV.[7] Variable-temperature photoluminescence experiments on *n*-type ZnO:N showed a more promising hole binding energy of ~200 meV,[8] a value that is comparable to that of Mg acceptors in GaN.[9] However, compensation by donors such as hydrogen impurities has prevented the realization of *p*-type ZnO. Magnetic resonance studies of ZnO have identified nitrogen acceptors,[10,11] but in the absence of laser excitation, the acceptors are negatively ionized (N^- or N_2^-).[11] First-principles calculations have shown that nitrogen acceptors may be compensated via the formation of defects such as oxygen vacancies,[12] zinc antisites, and complexes with zinc interstitials or N_2 molecules.[13–15]

Finding a doping scheme that results in a high acceptor concentration, while avoiding the formation of compensating defects, will be essential for the realization of practical ZnO-based devices. One possible route to *p*-type conductivity is to first introduce neutral N-H complexes into ZnO. In contrast to N acceptors, neutral N-H complexes would not drive the formation of compensating *n*-type defects. The hydrogen could then be removed by postgrowth annealing, as is currently done with GaN:Mg.[16,17] In this Brief Report, we present evidence that we have successfully introduced N-H complexes into ZnO during growth by using ammonia (NH_3) as an ambient.

Chemical vapor transport (CVT) was used to grow polycrystalline ZnO, with graphite as a transport agent.[3,18] The source materials were 1.5 g ZnO aggregate and 2.0 g high-purity graphite [99.99+(%), Sigma-Aldrich].[19] The ZnO aggregate was created by mixing ZnO micropowder (99.9%, Sigma-Aldrich) with high-purity low-contaminant water. The water was then boiled away until dry aggregated pieces of ZnO were left behind, in which some water most likely remained. This was done to decrease the surface area of the ZnO source material, thereby decreasing the growth rate and increasing crystal quality. The materials were placed at one end of a fused-silica ampoule (~12 cm long). The ampoule was backfilled with 0.5 atm anhydrous NH_3 and sealed with a hydrogen-oxygen torch. The sealed ampoule was then placed in a horizontal tube furnace, and the end containing the source materials was heated to ~950 °C. Polycrystalline ZnO grew on the opposite end of the ampoule, which was ~50 °C cooler. The ampoule was maintained at a constant temperature for approximately 72 h, and then cooled to room temperature over 3 h. This procedure resulted in a polycrystalline sample with a reddish color, evidence of Zn-rich growth conditions.[18,20] The average thickness of the sample was roughly 1 mm.

Fourier-transform infrared spectroscopy was performed with a Bomem DA8 spectrometer and a Janis STVP continuous flow liquid-helium cryostat with ZnSe windows. At liquid-helium temperatures ($T \sim 10$ K), we observed an IR absorption peak at a frequency of 3150.6 cm^{-1} (Fig. 1). The full width at half maximum (FWHM) of the peak was 2.3 cm^{-1} at an instrumental resolution of 1 cm^{-1}. At room temperature, the peak has a slightly lower frequency (3147.7 cm^{-1}) and larger width (8 cm^{-1}). The shift and broadening are due to the interaction between the local vibrational mode (LVM) and lattice phonons.[21] The frequency of the LVM (3150.6 cm^{-1}) is similar to the bond-stretching frequency of N-H complexes in ZnSe:N (3194 cm^{-1}) (Ref. 22) and GaN:Mg (3125 cm^{-1}).[23] ZnO samples grown in a N_2 or Ar ambient did not exhibit the peak at 3150.6 cm^{-1}.

To verify that this peak was due to hydrogen, a ZnO sample that showed the 3150.6 cm^{-1} peak was annealed in deuterium (D_2) gas at a temperature of 730 °C for 70 h, resulting in the partial substitution of D for H. This sample

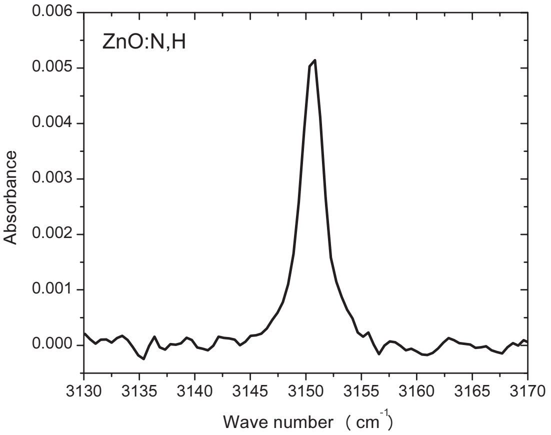

FIG. 1. IR spectrum of N-H complexes in ZnO at liquid-helium temperatures.

showed a peak at 2339.7 cm^{-1} at liquid-helium temperatures, with an instrument-limited FWHM of 1 cm^{-1} (Fig. 2). The isotopic frequency ratio of these two modes is $r=\nu_{\mathrm{H}}/\nu_{\mathrm{D}}=1.3466$, in good agreement with that of ZnSe:N,H ($r=1.348$) (Refs. 22 and 24) and GaN:Mg,H ($r=1.3464$).[23] A smaller width of the N-D mode as compared to the N-H mode was also observed in GaN:Mg. This linewidth narrowing may result from the smaller vibrational amplitude of deuterium, which leads to smaller coupling to the lattice and, therefore, an increase in lifetime.[25]

The observed ZnO:N,H vibrational frequency is in good agreement with first-principles calculations. Vienna *ab initio* simulation package (VASP) calculations that use the local density approximation and ultrasoft pseudopotentials showed that the total energy is minimized when hydrogen forms a bond with nitrogen in an antibonding configuration, roughly perpendicular to the *c* axis (Fig. 3).[26] The calculated N-H bond-stretching mode frequency was 3070 cm^{-1}, in good agreement with our experimental value. Fritz-Haber Institute codes (FHI98), which use different pseudopotentials than the VASP codes, resulted in a bond-stretching frequency of 3117 cm^{-1}. This value agrees even better with experiment.

In order to confirm our assignment, we used ammonia that was enriched with 10% $^{15}\mathrm{NH}_3$ (Sigma-Aldrich) as an ambient during CVT growth. However, since this ammonia was not “anhydrous,” it presumably contained trace amounts of oxygen that counteracted the Zn-rich growth conditions. The sample that resulted from this growth was colorless and did not have the reddish color of the previous samples. IR spectroscopy of this sample did not reveal the absorption peak at 3150.6 cm^{-1}, even after annealing in H_2 gas.

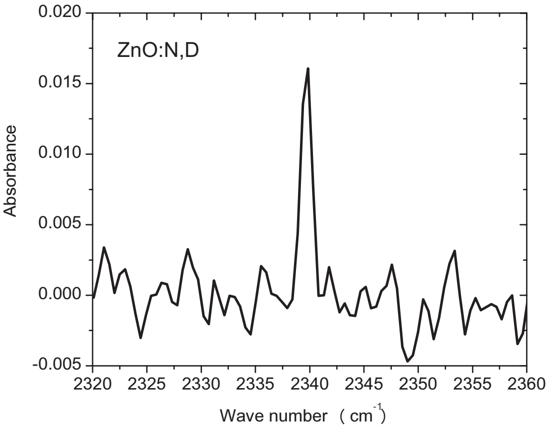

FIG. 2. IR spectrum of N-D complexes in ZnO at liquid-helium temperatures.

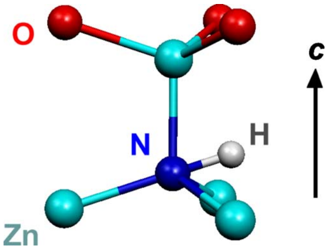

FIG. 3. (Color online) Schematic diagram of the N-H complex in ZnO from first-principles calculations (Ref. 26).

To create Zn-rich growth conditions with the isotopically enriched ammonia, we added ~0.01 g of Zn to the source material. The resulting crystal was red in color. IR spectroscopy showed the peak at 3150.6 cm^{-1} along with a smaller absorption peak located at 3144.1 cm^{-1} (Fig. 4). The peak at 3144.1 cm^{-1} is attributed to ^{15}N-H complexes, where the larger mass of ^{15}N as compared to ^{14}N results in a slightly lower vibrational frequency. The observation that Zn-rich (O-poor) growth conditions enhance the incorporation of N-H complexes is consistent with the idea that N-H pairs occupy oxygen vacancies.

The N-H frequencies were determined by peak fits to Lorentzian line shapes. During the least-squares fitting routine, the peak widths were constrained to be equal and the ratio of the peak areas was constrained to be 9:1, the isotopic composition of the ammonia gas. The result of the fit is shown by the dashed line in Fig. 4. According to a simple diatomic model, the vibrational frequency of the N-H complex is given by[27]

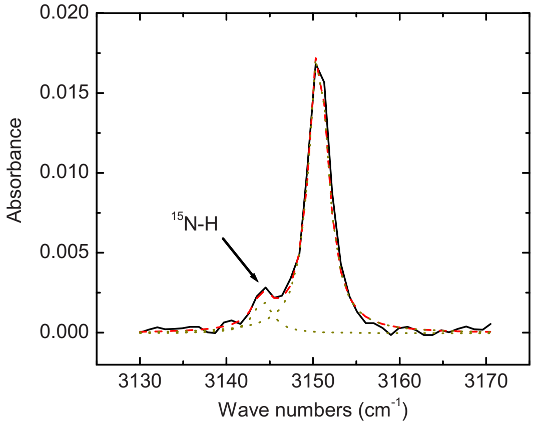

FIG. 4. (Color online) IR spectrum of N-H complexes in ZnO grown in an isotopically enriched ambient of 10% $^{15}\mathrm{NH}_3$+90% $^{14}\mathrm{NH}_3$. An absorption peak due to ^{15}N-H complexes is indicated by the arrow.

$$\upsilon = \sqrt{k(1/m + 1/\chi M)}, \tag{1}$$

where m and M are the masses of hydrogen and nitrogen, respectively, and χ is an empirical constant that accounts for the vibration of the other atoms in the vicinity of the N-H complex. From the observed ^{14}N-H and ^{15}N-H frequencies, we derived a value of $\chi = 1.105 \pm 0.05$. The fact that $\chi \sim 1$ indicates that the N-H mode is highly localized and the neighboring atoms have small vibrational amplitudes.

The ^{15}N-H peak at 3144.1 cm^{-1} unambiguously establishes that our observed IR absorption peaks arise from N-H complexes. This study appears to resolve the disagreement about the assignment of ZnO:N,H modes, with different researchers reporting LVM frequencies near 2400 cm^{-1},[28] 3000 cm^{-1},[26] and 3100 cm^{-1}.[29] None of those studies included an observation of N-D or ^{15}N-H complexes, allowing us to speculate that the reported peaks arose from carbon-hydrogen or oxygen-hydrogen vibrations. While it is conceivable that there are alternate nitrogen-hydrogen structures in ZnO, isotopic substitution or other quantitative experiments would be required to verify their existence.

To test the stability of the N-H complexes, we performed a series of isochronal anneals in open air. A ZnO sample that contained N-H complexes was annealed between 200 and 800 °C for 1 h at each temperature. The N-H peak height (at room temperature) is plotted as a function of annealing temperature in Fig. 5. Since the sample was polycrystalline, the thickness was not well defined, resulting in large errors in the peak height determination. Nonetheless, it is apparent that the N-H complexes dissociate in the temperature range of 600–800 °C. To quantify this process, we modeled the data using first-order kinetics. The rate of dissociation is given by

$$1/\tau = \upsilon_0 \exp(-E_A/kT), \tag{2}$$

where ν_0 is an attempt frequency, E_A is an activation energy, k is Boltzmann's constant, and T is the annealing temperature (K). The number of N-H complexes remaining after an anneal is

$$N = N_0 \exp(-t/\tau), \tag{3}$$

where N_0 is the number of N-H complexes prior to the anneal and t is the annealing time; in this case, $t=1$ h. The parameters that fit the data best are $E_A = 3.3$ eV and $\nu_0 = 3 \times 10^{13}$ Hz. Since we did not apply a bias during annealing, hydrogen retrapping may result in an overestimate of the activation energy. Nonetheless, the N-H complexes are much more stable than hydrogen donors, which we observed to decay with an activation energy of 1 eV.[30] We did not observe statistically significant changes in the free-carrier absorption, suggesting that the ZnO samples remained n-type after annealing.

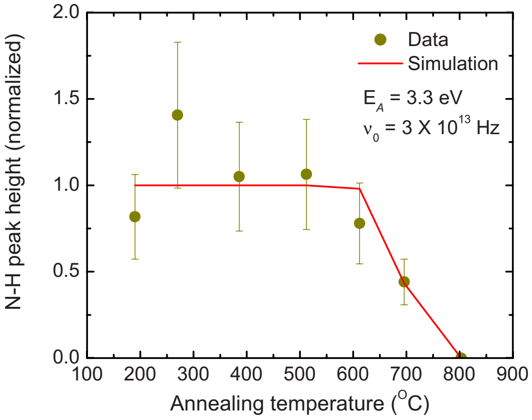

FIG. 5. (Color online) Peak height of the N-H mode as a function of annealing temperature for a series of isochronal anneals (1 h each). The solid line is a fit to a model assuming first-order dissociation kinetics.

In conclusion, we have spectroscopically identified nitrogen-hydrogen complexes in ZnO grown by chemical vapor transport in an ammonia ambient. The experimental results are in good agreement with first-principles calculations, which predict that hydrogen should form a bond with nitrogen and reside in an antibonding location. The introduction of N-H complexes could provide the first step toward doping with N acceptors. By optimizing the growth and annealing conditions, it may be possible to activate large concentrations of N acceptors and achieve reliable p-type conductivity in ZnO.

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