

Vibrational Spectroscopy of Na–H Complexes in ZnO

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Sodium acceptors were diffused into ZnO bulk single crystals to a depth of $\sim 1 \mu\text{m}$, with a near-surface concentration of $\sim 10^{18} \text{ cm}^{-3}$. An O–H local vibrational mode (LVM) was observed at 3304 cm^{-1} , at a temperature of 9 K, in hydrogenated samples. The LVM is attributed to an O–H bond-stretching mode adjacent to a Na acceptor. When deuterium substitutes for hydrogen, a peak is observed at 2466 cm^{-1} . The isotopic frequency ratio is similar to values found in other hydrogen complexes. In the deuterated sample, a sideband at 2461 cm^{-1} is attributed to a Fermi resonance.

Key words: ZnO, infrared, acceptor, SIMS

Demand for white light-emitting diodes (LEDs),¹ high-power solid-state emitters, and lasers for use in displays, illumination, and optical storage has fueled research on wide-bandgap semiconductors. GaN, with a 3.42 eV bandgap at room temperature,² is a preferred material for optoelectronic applications. Wurtzite zinc oxide (ZnO), a wide-bandgap semiconductor with a 3.37 eV direct gap at room temperature,³ has emerged as a possible competitor. ZnO has several potential advantages over GaN. With a 60 meV exciton binding energy,⁴ ZnO is a more efficient emitter than GaN (25 meV exciton binding energy) at room temperature. Large ZnO wafers can be purchased for epitaxial growth, and wet chemical processing is straightforward. A problem with ZnO is that, while it can easily be made *n*-type, it is difficult to dope *p*-type in a reliable and controlled way. There are several reports on *p*-type doping with group IA and group V elements.^{5–7} However, reproducibility and reliability of *p*-type doping remain controversial.^{8,9}

Recent theoretical^{10,11} and experimental¹² studies showed that nitrogen is a deep acceptor, with a level $\sim 1.3 \text{ eV}$ to 1.7 eV above the top of the valence band, and is therefore unsuitable for *p*-type doping. Sodium is a potential acceptor dopant in ZnO. In addition to behaving as deep acceptors,

Meyer et al.¹³ reported that Li and Na, incorporated either by diffusion or during thin-film growth, can also result in relatively shallow acceptors. Several other groups have reported first-principles calculations for column IA impurities (Li, Na, and K) in ZnO.^{14,15} Park et al.¹⁶ performed calculations for substitutional Li, Na, and K in ZnO, reporting ionization energies of 0.09 eV, 0.17 eV, and 0.32 eV, respectively. Du and Zhang,¹⁷ using hybrid density-functional calculations, found acceptor levels near 0.3 eV for Li and Na.

In the present study, sodium acceptors and sodium–hydrogen complexes were investigated experimentally. Melt-grown cermet ZnO single crystals¹⁸ were used in this work. Alkali-metal dispensers from SAES Advanced Technology were used as the alkali-metal source. The alkali-metal-generating material is a mixture of an alkali-metal chromate with a reducing agent. The chromates used were anhydrous alkali-metal salts of chromic acid with general formula Me_2CrO_4 , where Me denotes an alkali metal (Li, Na, K, Rb or Cs). Sodium dispensers of 50 mm slit length with 6 mg cm^{-1} yield were used for sodium doping.

Before sodium diffusion, ZnO crystals were annealed in oxygen at 900°C for 30 h in a sealed silica ampoule that was evacuated and baked. The oxygen pressure was ~ 200 torr at room temperature prior to sealing the ampoule. Selim et al.¹⁹ showed that zinc vacancies are created by oxygen

annealing. For sodium doping, oxygen-annealed ZnO crystals were placed on top of two sodium dispensers in a silica ampoule. The ampoule was evacuated, baked, and then sealed. The sodium doping was done at a temperature range of 600°C to 700°C for ~ 15 h in a tube furnace.

Secondary-ion mass spectrometry (SIMS) was performed at Evans Analytical Group (EAG) to examine the incorporation and concentration of sodium dopants. SIMS depth profile measurements on two sodium-doped and activated ZnO samples (cermet-A and cermet-B) are shown in Fig. 1. These SIMS measurements show the depth profile of sodium up to ~ 1 μm in the ZnO samples, with a near-surface concentration of $\sim 10^{18}$ cm^{-3} . The Na detection limit was $> 5 \times 10^{15}$ atoms cm^{-3} .

Infrared (IR) absorption spectra were obtained with a Bomem DA8 vacuum Fourier-transform infrared spectrometer equipped with a global light source, KBr beam splitter, and liquid-nitrogen-cooled indium antimonide (InSb) detector. A Janis closed-cycle helium cryostat system was used to maintain the samples at low temperatures. For hydrogen and/or deuterium annealing, the crystals were annealed at 500°C in a sealed silica ampoule that was filled with 500 torr H_2 or D_2 gas prior to sealing. The annealing was performed in a horizontal tube furnace for 60 h for hydrogen and 72 h for deuterium.

In hydrogenated samples (cermet-C), an O–H local vibrational mode (LVM) was observed at 3304 cm^{-1} at a temperature of 9 K (Fig. 2). This LVM frequency is in good agreement with theoretical predictions for the sodium–hydrogen complex, with hydrogen in an antibonding configuration (AB_\perp , 3389 cm^{-1}).²⁰ In deuterated samples (cermet-D), we found a peak at 2466 cm^{-1} , with a sideband at 2461 cm^{-1} (Fig. 2). The isotopic frequency ratio is $r = \nu_{\text{H}}/\nu_{\text{D}} = 1.339$, similar to values found in many

hydrogen/deuterium-related complexes.²¹ Hydrogenated samples that were not Na doped showed the O–H mode at 3326 cm^{-1} , attributed previously to interstitial hydrogen donors,²² but did not show the mode at 3304 cm^{-1} .

We tentatively attribute the sideband to a Fermi resonance between the O–D stretch mode and the third harmonic of the O–D wag (E) mode. According to first-principles calculations,²⁰ the ratio of the O–D stretch and wag mode frequencies is very close to three ($2469/826 = 2.99$). The accidental degeneracy between the $n = 3$ wag mode and fundamental stretch mode results in a strong anharmonic interaction. This interaction gives the $n = 3$ wag mode some “stretch” character, enabling it to absorb IR light. The calculated ratio of the O–H stretch and wag modes is far from three ($3389/1033 = 3.28$), resulting in negligible resonance. This isotopic difference is due to the larger relative motion of oxygen in the wag mode as compared with the stretch mode. Since oxygen participates more in the wag vibration, the effect of replacing hydrogen with deuterium is less than that for the stretch mode. Examples of Fermi resonance have been observed previously in Si²³ and AlSb.²⁴ However, neither of these cases involves the *third* harmonic of a wag mode.

The hydrogenated sample (cermet-C) was oxygen annealed in steps at 500°C, 700°C, and 800°C for 45 min each, with photoluminescence (PL) measurements taken after each annealing step. No donor–acceptor pair (DAP) emission was detected in these spectra. After oxygen annealing at 900°C for 45 min, a DAP emission at ~ 410 nm to 415 nm was observed (Fig. 3) while the LVM at 3304 cm^{-1}

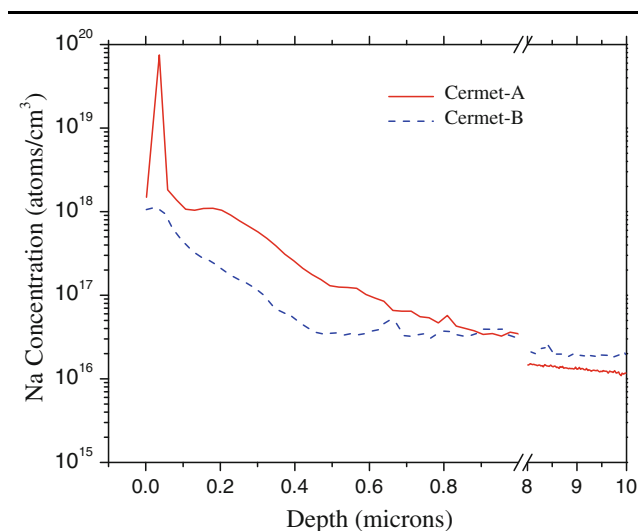


Fig. 1. (Color online) SIMS depth profiles for two ZnO samples. Sodium was diffused to depth of ~ 1 μm .

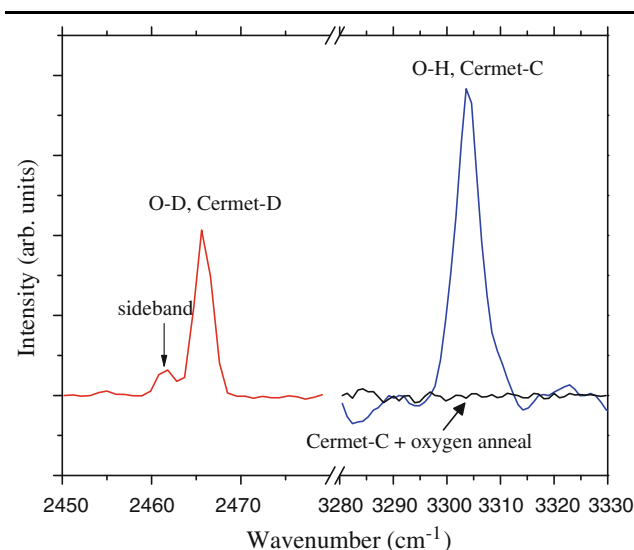


Fig. 2. (Color online) IR absorption spectra of the sodium–hydrogen complex in ZnO at 9 K. These samples were sodium doped, followed by hydrogen/deuterium annealing. The 3304 cm^{-1} peak is attributed to an O–H and the 2466 cm^{-1} peak is attributed to an O–D stretch LVM, with a sideband at 2462 cm^{-1} . The 3304 cm^{-1} peak disappeared after oxygen annealing at 900°C.

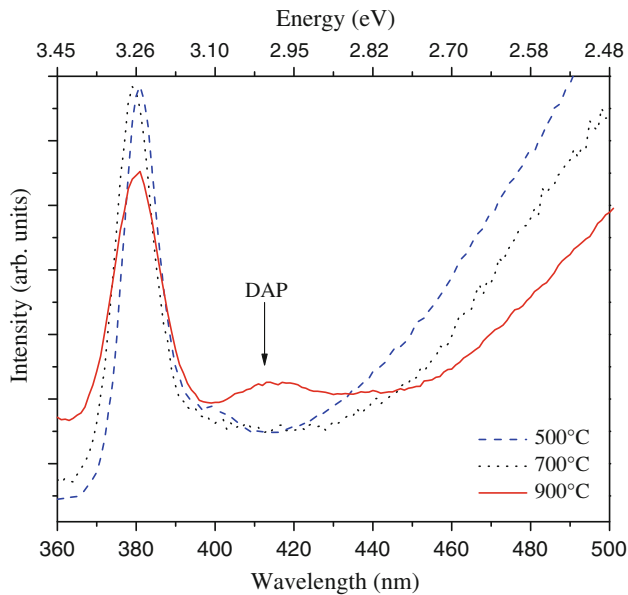


Fig. 3. (Color online) Photoluminescence DAP emission at ~ 414 nm observed at room temperature after oxygen annealing the ZnO (cermet-C) sample for 45 min duration.

disappeared (Fig. 2). This DAP line is attributed to a transition from shallow donor to a Na acceptor.¹³ Room-temperature Hall measurements showed semi-insulating behavior of the sample, consistent with activation of the sodium acceptors.

Our results may be compared with those for lithium acceptors,^{25,26} which are also passivated by hydrogen.^{27,28} The lithium–hydrogen complex is highly stable, annealing out only at temperatures above 1100°C .²⁹ First-principles calculations³⁰ predicted that sodium–hydrogen complexes have a lower dissociation activation energy (1.02 eV) than lithium–hydrogen complexes (1.88 eV). Our experimental annealing temperature of 900°C supports this prediction, at least qualitatively.

In conclusion, sodium acceptors are passivated by hydrogen, resulting in an O–H bond-stretching vibrational mode at 3304 cm^{-1} . The O–D stretch mode shows evidence of a Fermi resonance with a third-harmonic wag mode. Sodium–hydrogen complexes are dissociated by annealing at 900°C . This dissociation leaves behind sodium acceptors, a process that could prove useful for *p*-type doping.

ACKNOWLEDGEMENTS

This work was supported by Positron Storage for Space and Missile Defense Applications Contract Number W9113M-09-C-0075, US Army Space and Missile Defense Command, and US Army, Army

Research Laboratory. M.D.M. acknowledges support from DOE Grant DE-FG02-07ER46386. We thank M. H. Weber for valuable discussions.

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