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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 ~1 μm, with a near-surface concentration of ~10^{18} 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 experimental[12] studies showed that nitrogen is a deep acceptor, with a level ~1.3 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 crystals[18] 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

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