

Hydrogen as a Dopant in Zinc Oxide

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Motivation—Zinc oxide, already a widely used electronic material, has the potential to become an important material for the fabrication of light emitting diodes for short wavelength and white light applications. Two principal problems persist which have stymied the use of this wide-bandgap semiconductor. The first is the lack of a reproducible method for p-type doping, and the second is the poor understanding of the "native dopant" which causes nominally pure ZnO to be always n-type. Recent calculations using density functional theory (DFT) have suggested that hydrogen, which is usually present when ZnO is grown by hydrothermal techniques, might be an important "accidental dopant" in this material.

Accomplishment—In order to make a quantitative connection between the amount of dissolved hydrogen and any observed changes in electrical properties of this material, we have annealed single crystal ZnO samples from several sources in H₂ and D₂ gas at 750°C and compared the observed changes in electron concentration and mobility with Nuclear Reaction Analysis and Secondary Ion Mass Spectrometry profiles of deuterium. In addition we studied the evolution of local vibrational modes of H-related defects before and after these anneals with Fourier Transform Infrared Vibrational Spectroscopy. This study is the first quantitative correlation of H/D densities with carefully measured electrical and optical properties of ZnO. We find that the amount of deuterium remaining in our gas-charged samples ranges from 3.6 to 5.5 x 10¹⁷ cm⁻³, substantially larger than the increase in conduction band electron densities deduced from Hall effect measurements. Our

modeling indicates that these gas treatments produce a hydrogen-related donor state at 0.036 ± 0.004 eV below the conduction band minimum (Fig. 1) and also cause significant increases in the measured conduction band electron mobility. Another key finding is the observation of a local vibrational mode of dissolved D at 2619 cm⁻¹ and an H analog at 3546 cm⁻¹. These modes are close to the DFT-predicted frequencies for D/H in a bond-centered position between zinc and oxygen. Using this mode as a measure of H content, we deduce that hydrogen is present in significant amounts in as-received samples but is not the "native donor". Using this optical indicator of H content and our modeling of electrical data, we conclude that all of the H in as-received ZnO is passivating acceptor impurities that are unintentionally incorporated during the growth process. When more H or D is deliberately added, it preferentially bonds to un-passivated acceptors, with the remaining amount functioning as an isolated shallow donor. This provides a convincing explanation for both the improved carrier mobilities and the discrepancy between the NRA-measured deuterium densities and the electrically active donor concentrations in our D₂ gas-charged samples.

Significance—These experiments have shown that hydrogen can play a key role in the electronic properties of ZnO. Since we find that hydrogen is present at the 10¹⁷ cm⁻³ level in most ZnO and it readily binds to acceptor impurities (effectively preventing them from donating holes to the valence band), great care must be taken to control the hydrogen content during growth of p-type ZnO layers for optoelectronic devices.

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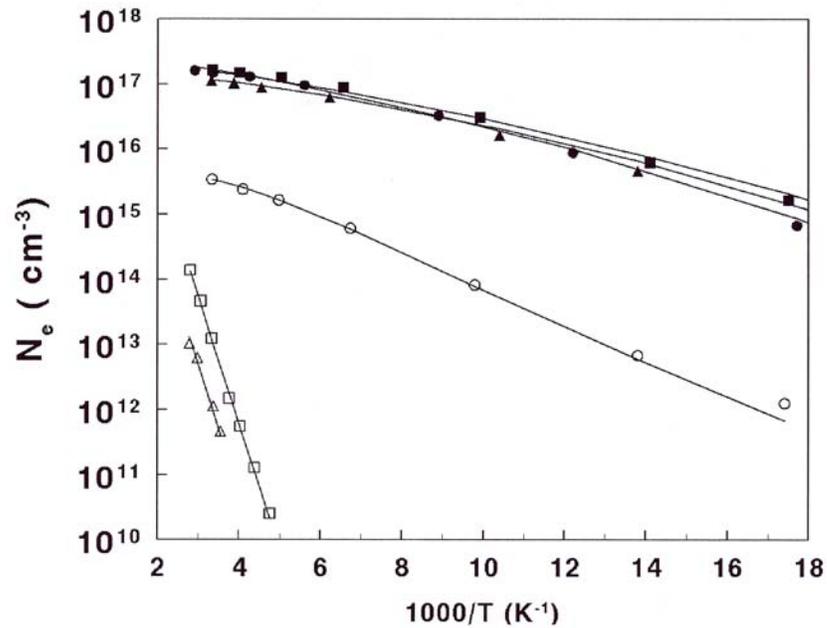


Figure 1. The electron concentration in ZnO from three different growers, plotted as a function of inverse temperature. Open symbols are data from as-received samples, filled symbols are data obtained after anneals in H_2 gas at $750^\circ C$. Hydrogen functions both as a shallow donor and as a passivator of pre-existing acceptors, raising the electron concentration in the material and reducing its variation with temperature. Lines are theoretical fits made to deduce donor and acceptor densities.

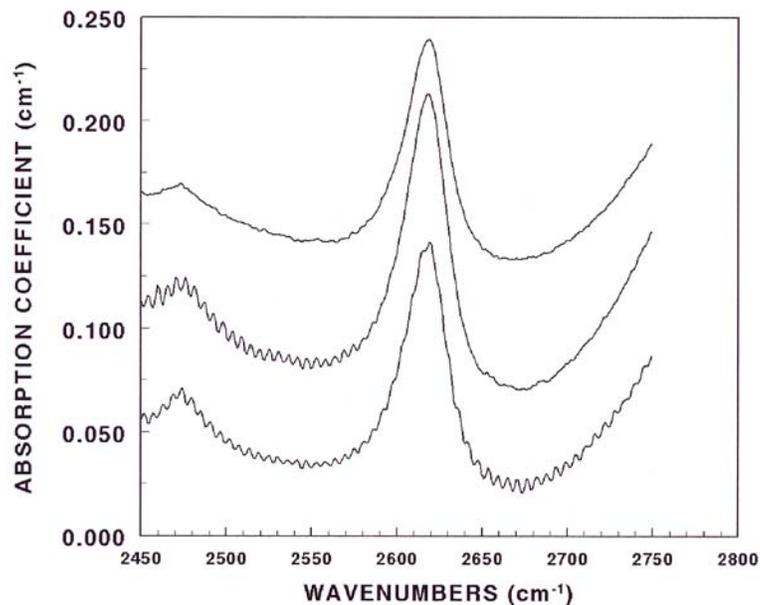


Figure 2. Local vibrational mode spectra of ZnO treated in D_2 gas at $750^\circ C$. The peak at 2619 cm^{-1} is consistent with theoretical predictions of the infrared absorption expected from a D atom bonded to oxygen in ZnO. The three spectra are from samples grown by different vendors.