Acceptors in ZnO nanocrystals

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While zinc oxide (ZnO) has potential for optoelectronic applications, the lack of reliable p-type doping remains a major challenge. We provide evidence that ZnO nanocrystals contain uncompensated acceptors. IR absorption peaks at liquid-helium temperatures suggest a hydrogenic acceptor with a hole binding energy of 0.4–0.5 eV. Electron paramagnetic resonance (EPR) measurements in the dark showed a resonance at g = 2.003, characteristic of acceptors that involve a zinc vacancy. An EPR resonance due to vacancy hydrogen complexes was observed after exposure to light. Given the lack of alternatives, vacancy complexes may provide a feasible route toward p-type conductivity. © 2011 American Institute of Physics. [doi:10.1063/1.3598411]

Zinc oxide (ZnO) has been gaining tremendous attention as an optoelectronics material, owing to its direct band gap of 3.4 eV and large exciton binding energy (60 meV). ZnO has been used as a buffer layer for growth of GaN-based devices, as a transparent conductive oxide has been used as a buffer layer for growth of GaN-based dots, and as a transducer for micro electrical-mechanical systems. Nanoscale ZnO is interesting for several reasons. Quantum confinement allows one to tune the band gap, as the dimensions of the nanocrystal approach the exciton radius (1.8 nm for ZnO). The high surface-to-volume ratio makes nanocrystals sensitive to the environment, useful for gas-sensing applications. Finally, ferromagnetic quantum dots could be used in high density storage devices.

The lack of reliable p-type doping has prevented ZnO from widespread use in optoelectronic applications. Proposed acceptor dopants include substitution of N on O sites, and group-I elements such as Li (Ref. 11) and group-IB elements such as Cu (Ref. 12) substituting on Zn sites. However, experimental studies have shown that Li and Cu are deep acceptors. Calculations have suggested that N, once thought to be a hydrogenic acceptor, is actually a deep acceptor with significant lattice relaxation. Recent experimental results are consistent with this deep-acceptor model. In this letter, we provide evidence that ZnO nanocrystals contain hydrogenic acceptors as grown. Analogous to the hydrogen atom, hydrogenic acceptors give rise to electronic transitions that can be observed in the IR.

ZnO nanoparticles were synthesized by solid-state pyrolytic reaction process. In this method, zinc acetate dihydrate [Zn(CH3COO)2·2H2O] and sodium hydrogen carbonate (NaHCO3) are reacted at 200 °C for 3 h in an open-air furnace. Details are given in Ref. 18. Transmission electron microscopy showed that the particles have an average diameter of ~20 nm. The nanopowder was pressed into pellets of thickness ~0.25 mm with a diameter of 7 mm. Low temperature (10 K) IR absorption spectra were obtained with a Bomem DA8 Fourier transform infrared spectrometer. A KBr beam splitter and InSb detector were employed for the spectral range of 1800–7000 cm−1, with an instrumental resolution of 2 cm−1. In order to remove hydroxyl related surface species, the sample was baked out at 323 K inside the cryostat under vacuum before cooling down to low temperature. Electron paramagnetic resonance (EPR) measurements were carried out with a Bruker 380E X-band spectrometer operating at 9.38 GHz and a sample temperature of 77 K.

Figure 1 shows an IR absorption spectrum for the as-grown ZnO nanoparticles. The IR absorption spectrum was calculated using absorbance=log10(I/I0), where I and I0 are the transmission spectra for no sample (blank) and an as-grown sample, respectively. A quadratic baseline was then subtracted from the absorbance spectrum. A series of peaks is observed in the energy range of 425–457 meV. This result is suggestive of a hydrogenic acceptor spectrum with a hole binding energy of 0.4–0.5 eV. Peaks did not shift in frequency for samples grown with deuterated precursors, which argues against the involvement of hydrogen. Na acceptor atoms were ruled out by growing nanocrystals using Li precursors, which showed the same set of lines.

The series of IR absorption peaks is similar to those observed in other II–VI compound semiconductors, such as shallow (Ref. 20) and deep (Refs. 21 and 22) acceptor levels.

FIG. 1. (Color online) Low temperature (10 K) IR spectrum of ZnO nanocrystals showing electronic transitions.

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in cubic ZnTe. The transition energies are explained in the framework of the theory of Baldereschi and Lipari. In this theory, within the spherical approximation, the acceptor Hamiltonian reduces to that of a hydrogen atom modified by a spherical “spin-orbit” term, which can be thought as a spin-3/2 particle in a Coulomb potential. When the cubic term in the Hamiltonian is included, the symmetry lowers to that of the point group Td. The wave functions of the holes are classified according to the irreducible representations of this point group.

For the wurtzite crystal structure of ZnO, the point-group symmetry is C_{3v}. The crystal field and spin-orbit coupling split the valence band into three bands labeled A, B, and C (Fig. 2). At low temperatures, the energy difference between A and B excitons has been reported to be 15 meV. As shown in Fig. 1, the sets of lines labeled a and b are offset by ~15 meV. We assign these transitions to excited states with holes originating from the A and B valence bands, respectively.

The envelope functions of the ground state have nonzero probability densities at the acceptor core, leading to a central-cell correction. However, the excited P states are less sensitive to central cell corrections and are best described by hydrogenic wave functions. In a single hole picture, the A valence band in C_{3v} symmetry gives rise to a hole wave function with C_{3v} symmetry (double group notation). The acceptor P wave functions belong to the representations \Gamma_1 \times \Gamma_4 = \Gamma_4 \text{ and } \Gamma_3 \times \Gamma_4 = \Gamma_4 + \Gamma_5 + \Gamma_6. The B valence band has Kramers doublet (\Gamma_5, \Gamma_6) symmetries, where \Gamma_5 and \Gamma_6 are degenerate in the absence of an applied magnetic field. Figure 2 shows the allowed acceptor levels and hole transitions, along with their assignments. The observation of five main IR peaks is in agreement with our group-theoretical analysis. The side bands of b1 and a2 could be due to a slight reduction in symmetry, from C_{3v} to C_3.

EPR measurements showed resonances at g = 1.96 and g = 2.003 in as-grown ZnO nanocrystals in the dark, prior to illumination by a xenon lamp (Fig. 3). The g = 1.96 resonance is associated with shallow donors. We attribute the resonance at g = 2.003 to hydrogenic acceptors. A new signal at g = 2.013 appears after illumination. This center is consistent with nonaxial V_{Zn}H complexes, which were observed previously in electron-irradiated, bulk ZnO after illumination with 325 nm laser light. The V_{Zn}H complexes are partially passivated Zn vacancies, with a hole residing on one of the nonaxial O atoms. Exposure to light transforms (V_{Zn}H)^-, which is EPR-inactive, to (V_{Zn}H)^0. The light also creates new centers near g = 2.003, which are attributed to axial V_{Zn}H.

In bulk ZnO, the EPR signatures for g = 2.003 acceptors only appear after illumination. This is because, in the dark, the acceptors are fully compensated by donors and are EPR-inactive. ZnO nanocrystals, in contrast, appear to contain uncompensated acceptors. There are two possible reasons for this. First, the nonequilibrium growth conditions may result in a high concentration of vacancy defects. Second, some of the nanocrystals may contain one acceptor and no donors, simply due to the small number of atoms in the nanocrystal.

In conclusion, we have studied defect properties of ZnO nanocrystals at low temperature using IR and EPR spectroscopy. The observed IR transition lines are consistent with a hydrogenic acceptor hole binding energy of 0.4–0.5 eV. EPR measurements show that the nanocrystals contain vacancy-hydrogen complexes (V_{Zn}H). Given the existence of these complexes, it is reasonable to speculate that the observed hydrogenic acceptor may be vacancy-related. While V_{Zn} and V_{Zn}H acceptors are deep, the acceptor level for the neutral vacancy (V_{Zn}^0) is predicted to lie 0.2 eV above the valence-band maximum. Our EPR measurements, however, did not detect the V_{Zn}^0 signature. A second possibility is a V_{Zn}-donor complex, which could contribute to the EPR resonance at g = 2.003. Considering the lack of suitable acceptor dopants in ZnO, defect complexes merit additional investigation.

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