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APPLIED PHYSICS LETTERS **86**, 171102 (2005)

Optical observation of donor-bound excitons in hydrogen-implanted ZnO

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(Received 20 December 2004; accepted 8 March 2005; published online 18 April 2005)

The optical and structural properties of H or He implanted ZnO were investigated using low temperature photoluminescence (PL) and infrared spectroscopy (IR). H implantation is shown to influence the relative luminescence intensities of the donor bound excitons, enhancing the 3.361 eV peak, and changing the overall intensity of the PL spectrum. PL from He implanted ZnO is used to demonstrate that implantation damage is partially responsible for the variations observed in the PL of H implanted ZnO. IR spectra show that the increase in the relative intensity of the 3.361 eV peak coincides with an appearance of the H vibrational mode in the ZnO lattice. Our results indicate that the implanted H forms O–H bonds at Zn vacancies, and that it is these defect complexes which give rise to the shallow donors participating in the observed bound-exciton luminescence at 3.361 eV. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1906330]

As-grown ZnO, in the nominally undoped state, typically exhibits *n*-type conductivity. In spite of intensive research, the origin of the *n*-type conductivity is still debated. It has been traditionally attributed to native defects in the ZnO.[1] However, both experimental and theoretical studies have not clearly demonstrated that there is a native defect which behaves as a shallow donor in ZnO. Recently, first-principles calculations have suggested that hydrogen acts as a source of *n*-type conductivity.[2] Consistent with these calculations, several studies using electron paramagnetic resonance, Hall effect measurements, and muon spin spectroscopy have shown that there is a shallow H-related donor level just below the conduction band.[3,4]

In this article, we investigate the effects of H implantation on the optical properties of ZnO using a combination of low temperature photoluminescence (PL) and multiple internal reflection infrared (MIR-IR) spectroscopies.

Commercially available ZnO single crystals were used in this work.[5] The (0001) surfaces were implanted with 6 keV H^+ at doses of 2×10^{13}, 3×10^{14}, and 5×10^{15} H/cm^2. At this energy the majority of the implanted H comes to rest at a depth between 40–110 nm, which is believed to be within the absorption and emission depth for PL. This is the significant difference between our study and previous work regarding the effect of H implantation in ZnO.[6,7] Due to the high implantation energies ranging from 100 keV to 1 MeV in previous studies, the implanted H resided much deeper than the optically active region and showed only the effect of implantation induced damage on the optical properties of ZnO. Half of the hydrogen-implanted samples were annealed in vacuum at 300 °C for 15 min. To evaluate the role of the implantation damage on the PL spectrum of ZnO, a companion set of room temperature implants was produced using 10 keV He^+ at a dose of 2.5×10^{13} /cm^2, which according to the stopping and range of ions in matter (SRIM) simulations[8] supplies the same amount of lattice damage as the 6 keV H^+ implantation at 3×10^{14} /cm^2. PL was excited using the 351 nm line from an Ar^+ laser and the emitted light was detected with a LN_2-cooled charge-coupled device camera. Infrared spectroscopy (IR) measurements in multiple internal reflection mode were performed at room temperature.

Figure 1 shows the change in the 4.2 K PL spectra for ZnO as a function of H implantation dose. The bound-exciton PL spectrum prior to implantation exhibits at least six narrow peaks with the strongest peak at 3.364 eV measuring about 1 meV full width at half maximum (FWHM), consistent with the previous work by Reynolds *et al.*[9] After H implantation, the relative intensity of PL peaks changed. The intensity of the 3.361 eV peak relative to that of the 3.364 eV peak increased for all doses. In addition, the overall PL intensity of the H implanted ZnO showed a nonlinear variation with respect to the H implantation dose. While the 2×10^{13} H/cm^2 implantation increased the overall PL intensity, the 3×10^{14} and 5×10^{15} H/cm^2 implantations decreased the intensity. The FWHM of the PL peaks increased with increasing H implantation dose, causing the well-resolved peaks observed in unimplanted ZnO to merge after

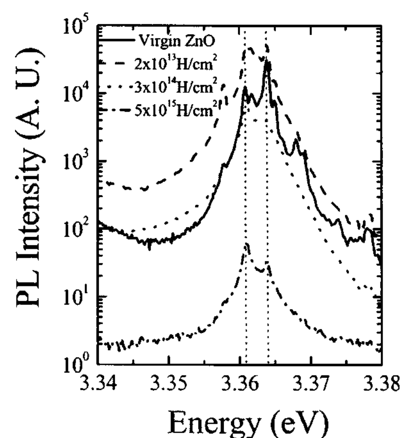

FIG. 1. PL spectra of unimplanted and 2×10^{13}, 3×10^{14}, and 5×10^{15} H/cm^2 H implanted ZnO measured at 4.2 K.

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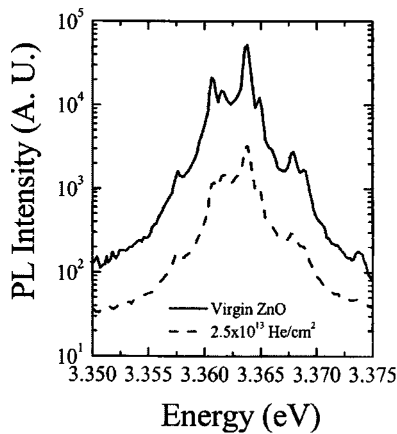

FIG. 2. PL spectra of He implanted ZnO measured at 4.2 K.

the 5×10^{15} H/cm^2 implantation leaving only two broad PL peaks at 3.361 and 3.364 eV. (See Fig. 1)

PL measurements were also performed for ZnO implanted with He. Since there is no chemical interaction between He and ZnO, changes in the PL spectra of this sample reflected ion implantation lattice damage. As shown in Fig. 2 a significant decrease in the PL intensity was observed following the He implantation, consistent with previous reports on the highly irradiated ZnO.[6,7] However, the relative intensity of the PL peaks remained unchanged and the peak at 3.364 eV still exhibited the maximum intensity.

To elucidate the effect of H passivation, PL spectra were also obtained for dehydrogenated ZnO. Figure 3 shows the PL spectra for ZnO that was implanted with 3×10^{14} H/cm^2 and then thermally annealed. A comparison with Fig. 1 shows that the relative peak intensities as well as the overall intensity of the PL changed after annealing; the relative intensity between the 3.361 and 3.364 eV peaks recovered to that of unimplanted ZnO and the overall PL intensity decreased to 15% of the PL intensity of H implanted ZnO. The overall decrease in intensity following annealing indicates that defect formation occurs as a result of dehydrogenation and alters the luminescence mechanism by enhancing the non-radiative energy transfer process.

The bonding nature between H and lattice damaged ZnO was investigated using MIR-IR for as-grown and 3×10^{14} H/cm^2 H implanted ZnO crystals. In Fig. 4, two broad bands, which are centered between 3330 and

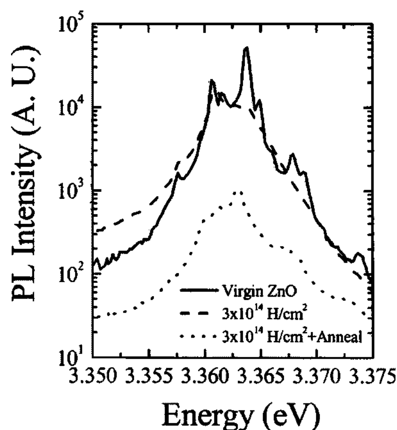

FIG. 3. PL spectra of as-implanted and 300 °C annealed ZnO for a dose of 3×10^{14} H/cm^2 measured at 4.2 K.

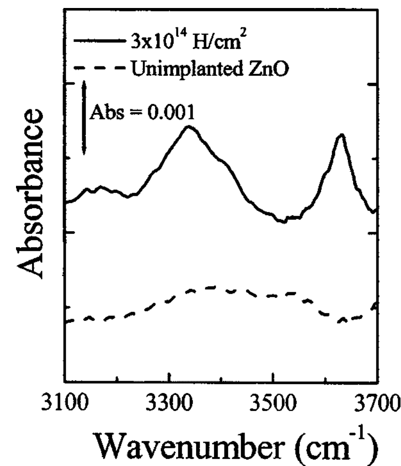

FIG. 4. Infrared (IR) spectra of as-grown and H implanted ZnO using MIR-IR geometry.

3630 cm^{-1} were observed for the H implanted ZnO. After dehydrogenation, the broad modes observed in the H implanted ZnO disappeared, demonstrating that the IR peaks above 3300 cm^{-1} were due to the local vibrations of H bound to ZnO.

These data show that implanted H has a complex effect on the luminescence of ZnO. H implantation under a critical dose promotes the radiative recombination process in ZnO and increases the overall intensity of luminescence. However, after annealing at 300 °C, the PL intensity of H implanted ZnO decreased by an order of magnitude, suggesting incomplete recovery or passivation of the lattice damage caused by ion implantation. While 300 °C is sufficient to allow the implanted H to escape partially from ZnO crystals,[10] it is not sufficient to remove most of the defects formed during ion implantation. This suggests that the decrease in PL intensity for annealed ZnO was due to H loss and the presence of unpassivated defects. Hence, the observed increase in PL intensity for 2×10^{13} H/cm^2 implanted ZnO is most likely due to passivation of grown-in or intrinsic defects. An increase in the overall PL intensity following H incorporation in ZnO has been observed by several groups. Ohashi *et al.* proposed that implanted H passivated the unintentionally doped acceptors and defects, leading to the increase in the PL intensity.[11] Polyakov *et al.*, however, attributed the increase of the PL intensity and electron concentration to either the presence of H shallow donors or H donor complexes bound to native defects.[12] Recently, Seager and Myer demonstrated that the incorporated H passivated most of the acceptor states and introduced a shallow donor level.[13] For H implantation at and above 3×10^{14} H/cm^2, a decrease in the total luminescence efficiency is observed, which we attribute to an increase in the concentration of the nonradiative centers produced by the ion implantation. It is apparent that irradiation defects contribute to the nonradiative process and suppress the luminescence process. However, it is noted that the shape of the PL spectra for the 3×10^{14} H/cm^2 implanted ZnO and the He implanted ZnO was different, although both conditions exhibit significantly decreased PL. The luminescence with the maximum intensity was found at 3.361 eV for H and at 3.364 eV for He implanted ZnO, respectively. This suggests that the change in the relative intensity of the 3.361 and 3.364 eV peaks cannot

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be exclusively attributed to the formation of irradiation defects.

As shown in Fig. 1, H implantation changed the relative intensities of the PL peaks, with the intensity of 3.361 eV peak becoming stronger relative to the 3.364 eV peak regardless of implantation dose or implantation damage. However, when implanted H started to be evolved from the ZnO crystals through annealing, the maximum intensity peak reverted to the 3.364 eV peak. Since both the 3.361 and 3.364 eV peaks are attributed to neutral donor bound excitons, these results suggest that the concentration of the donors responsible for the luminescence at 3.361 eV is very sensitive to the presence of hydrogen.

The IR peaks observed at 3330 and 3630 cm^{-1} in H implanted ZnO (Fig. 4) provide additional support for H being a shallow donor. Based on recent experimental observations together with predictions from first-principles calculations, the mode ranging from 3300 to 3400 cm^{-1} was assigned to a O–H bond where H occupies a Zn vacancy or an antibonding configuration, and the mode ranging from 3600 to 3700 cm^{-1} was assigned to an interstitial H atom in a bond centered (BC) site.[13–15] Our observation in the present work of two modes centered at 3330 and 3630 cm^{-1} is consistent with these previous reports, and indicates H bonding occurs in the H implanted ZnO. The simultaneous relative increase in the 3.361 eV luminescence peak and the appearance of the H vibration modes in ZnO indicates that implanted H that becomes chemically bonded to the ZnO lattice is responsible for the recombination of donor-bound excitons, and that this recombination is the source of the 3.361 eV PL peak.

A remaining question is the bonding configuration of the H in H implanted ZnO that gives rise to the 3.361 eV PL peak. It has already been established that the 3.364 eV PL peak is due to hydrogen-related-donor-bound excitons. This conclusion is based on several factors including an observed correlation between the 3.364 eV PL peak intensity and increased *n*-type conductivity in hydrogenated ZnO[16,17] and the fact that this peak is predominately observed in ZnO crystals that have been grown in or treated with hydrogen. However, ZnO consistently exhibits strong *n*-type conductivity and a 3.361 eV PL peak even when grown in low hydrogen environments. Still, both the 3.361 and 3.364 eV PL peaks are sensitive to dehydrating thermal treatments. The observed intensity reduction of these peaks following a high temperature anneal,[9,18] further suggests that H participates in both the 3.364 and 3.361 eV luminescence.

Van de Walle has shown that two kinds of hydrogen bonding can act as a shallow donor in ZnO: H in the bond-centered (BC) configuration and H bound to native defects.[2] First-principles and experimental studies of native defects in ZnO have predicted that the most stable (lowest formation energy) native defect in ZnO is the Zn vacancy,[19,20] which together with Van de Walle's findings suggest that the most likely H - native defect responsible for the 3.361 eV luminescence is the Zn vacancy–H complex. Structural defects in ZnO, such as Zn and O vacancies are expected to behave as deep acceptors and deep donors, respectively. However, H in a Zn vacancy bonds with surrounding oxygen atoms. The strength of the O–H bond in ZnO greatly reduces the energy for forming a hydrogen donor (i.e., H^+ formation), making a Zn vacancy–H complex act as a shallow donor. Here, it is worth recalling that H implantation naturally creates defects, such as vacancies and interstitials, and that the intensity of the 3.361 eV PL peak relative to that of the 3.364 eV PL peak was observed to increase for only H implanted ZnO and not for He implanted ZnO. We thus conclude that H forms defect complexes with native or implantation induced Zn vacancies and is responsible for the 3.361 eV PL peak while H in the BC configuration causes the 3.364 eV PL peak in ZnO as suggested by previous studies.

The Los Alamos portion of this work has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences. We also thank D. Wayne Cooke, G. Cantwell and B. Haskins for their discussion and help. Financial support provided to OSU by the NSF under Grant No. DMI-0100318 and the Oklahoma Center for the Advancement of Science and Technology are greatly appreciated.

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