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Photoluminescence of He-implanted ZnO

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Abstract

A study of the effects of ion-implanted He^+ on the 4.2 K photoluminescence (PL) of ZnO is presented. This investigation is motivated by the need to further understand the effects of damage resulting from the implantation process on the PL of ZnO. For this study, 10 keV He^+ ions were implanted at a dose of $2.5x10^{13}/cm^2$ in the (0001) Zn-terminated surface. The implantation process is seen to reduce the overall luminescence efficiency, although the number and relative intensities of the bound-exciton peaks are observed to be similar to that of unimplanted ZnO. The 4.2 K PL of the implanted surface exhibits a broad orange/red peak near 1.86 eV nm and is attributed to damage introduced during the implantation process. This peak is identified as donor-acceptor pair (DAP) luminescence with a thermal activation energy of 11 meV. The 1.86 eV peak is not observed for H-implanted ZnO suggesting that H passivates the implantation-induced defects responsible for this luminescence.

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1. Introduction

ZnO, with an exciton binding strength of 60 meV [1] and the recent successful demonstration of p-type doping [2], exhibits potential for use in short wavelength light emitters. Ion implantation has played an important role in the continued development of ZnO-based devices. Examples include ion-implanted nitrogen doping for the realization of p-type material [3], and ion bombardment for electrical isolation [4]. Ion implantation has also been used to investigate the role of hydrogen as a shallow donor in ZnO [5]. In each case, lattice damage resulting from the implantation process has been shown to have an undesirable effect on the optoelectronic properties.

Studies of ion-implantation-induced damage in ZnO include the work of Kucheyev et al. [6] who investigated structural defects of single-crystal material implanted with 60 keV ^{28}Si and 300 keV ^{197}Au ions using Rutherford backscattering/channeling (RBS/C) spectrometry, cross-sectional transmission electron microscopy, x-ray photoelectron spectroscopy and atomic force microscopy, and Sonder et al. [7] who reported annealing effects on RBS/C and secondary ion mass spectroscopy of Bi-, Cr-, and Mn-implanted ZnO. Photoluminescence (PL) has also been widely used to characterize ion-implanted ZnO, however, the effects of implantation-induced damage using chemically inert He ions has not been addressed.

The present work builds on our previous study which focused on the effects of H-implantation on the PL of ZnO [8]. In this study, we investigate the low-temperature and temperature-dependent PL of He-implanted ZnO. Since there is no chemical interaction between He and ZnO, differences observed in the PL spectra provide an indication of ion-implantation-induced lattice damage.

2. Experimental

Wurtzite structure ZnO produced by Eagle-Picher and grown by the seeded chemical vapor transport method [9] was used in the study. Ion implantation was performed on a chemo-mechanically polished (0001) ZnO surface. One half of the surface was implanted with 10 keV He^+ ions at a dose of 2.5 x $10^{13}/cm^2$. To investigate the effect of ion species on the PL of implanted ZnO, the other half of the sample was implanted with 6 keV H^+ ions at a dose of 3 x $10^{14}/cm^2$. According to the Stopping and Range of Ions in Matter simulations [10], these two implants are expected to introduce the same amount of lattice damage. PL was excited using the 351 nm (3.532 eV) line from an Ar^+ laser and the emitted light was dispersed by a 0.5 m monochromator and detected with a LN_2-cooled CCD camera. The near-band-edge (NBE) luminescence was dispersed by a 2400 g/mm diffraction grating with a resolution of 0.5 meV at 3.37 eV while the lower energy (1.4-2.8 eV) spectra were collected using a 1200 g/mm grating. The sample temperature was varied using a liquid helium continuous flow optical cryostat and luminescence was excited with the electric field vector perpendicular to the optical axis of the sample ($\mathbf{E}\perp\mathbf{c}$).

3. Results and discussion

Figure 1 compares the 4.2 K NBE PL of He-implanted ZnO (solid line) to that of an unimplanted surface (dotted line). PL of the unimplanted surface exhibits at least six sharp bound-exciton luminescence peaks. Reynolds et al. [11] in a PL study of vapor-phase grown ZnO identified these peaks as excitons bound to defect complexes which simulate neutral donors. After implantation, several differences in the PL are observed. First, the bound-exciton luminescence intensity is reduced more than an order of magnitude. This result is consistent with the results of Kucheyev et al. [12] who reported similar quenching of bound-exciton luminescence for ion-implanted GaN. Second, although the overall shape of the spectrum is similar to that of the unimplanted surface, small differences in the relative intensities of the bound-exciton peaks can also be seen. Both observations are likely the result of nonradiative centers introduced during the implantation process.

In addition to the differences observed in the NBE PL, the lower-energy region (< 2.8 eV) of the PL spectrum is also seen to be influenced by He^+ implantation, as shown in Fig. 2. Specifically, the PL of the implanted surface, curve (a), exhibits a broad orange/red peak near 1.86 eV, which is not observed for the unimplanted surface, curve (b). The sharp peaks near 1.6 eV are second order diffraction of the NBE luminescence. The full width at half maximum (FWHM) of the 1.86 eV peak at 4.2 K is about 420 meV. This large width is most likely the result of strong electron-lattice interaction. Based on the presumed electrical inactivity of He in ZnO and in light of the fact that the 1.86 eV luminescence is not observed in PL of the unimplanted surface, we attribute this peak to damage introduced during the implantation process. Similar damage-related, broad luminescence peaks have been reported for ZnO [13, 14].

Temperature-dependent PL was used to further investigate the nature of the 1.86 eV luminescence. Figure 3 shows PL spectra between 1.4-2.8 eV recorded at (a) 10 K, (b) 30 K, (c) 50 K, (d) 77 K, and (e) 150 K for He-implanted (0001) ZnO. The peak maximum is observed to shift to higher energy with increasing temperature. Based on this, we conclude that the 1.86 eV peak is the result of donor-acceptor pair (DAP) recombination. Studies have routinely reported blue shifts of DAP luminescence with increased temperature for other materials such as GaN [15] and GaS [16]. We estimate a shift of about 170 meV for an increase in temperature from 4.2 K to 150 K. This large shift may be attributed to a change in the PL mechanism from DAP to free-to-bound (i.e., either free-electron-to-acceptor or donor-to-free-hole) recombination. The nature of the donors and acceptors is uncertain and requires further study. The inset to Fig. 3 shows the normalized temperature-dependent total PL intensity (peak intensity times FWHM) of the 1.86 eV DAP peak. The temperature dependence of the total intensity was fitted according to [17]:

$$I(T)/I(0) = [1+ C\exp(-E_A/k_B T)]^{-1}$$

where E_A is the thermal activation energy for the shallowest trapped carriers (either donors or acceptors) and C is a temperature-independent constant. Using a least-squares routine, the best fit was obtained for $E_A = 11$ meV and $C = 54$. The small thermal activation energy suggests the possibility of a more complex luminescence mechanism such as two-donor, deep-acceptor recombination [18] or shallow-donor, deep-donor (acceptor) luminescence [19]; however, further study is required.

Figure 4 provides a comparison of the 4.2 K PL for the implanted surfaces in this study. Shown are the spectra near 1.86 eV for (a) He- implanted and (b) H-implanted ZnO. The 1.86 eV DAP peak is clearly observed only for the He-implanted surface, however there does appear to be a slight peak for the H-implanted surface near 1.86 eV. H has been shown to passivate defects in ZnO [20]. Based on this and in light of the fact that the 1.86 eV peak is not observed for the similarly damaged H-implanted surface, we conclude that the ion-implantation-induced damage is passivated by H.

Conclusions

Ion implantation of (0001) ZnO using 10 keV He^+ at a dose of 2.5 x $10^{13}/cm^2$ is seen to significantly affect the PL response. Nonradiative centers introduced during the implantation process result in severely quenched bound-exciton PL intensity, however the relative intensities of each of the peaks is only slightly affected. In addition to the nonradiative processes, ion-implantation-induced damage is also seen to introduce a new 4.2 K radiative transition near 1.86 eV. The temperature dependence of the energy of this peak suggests that it is the result of DAP recombination. Further study of the temperature dependence of the intensity of this peak results in a thermal activation energy of about 11 meV. From a comparison of the 4.2 K PL spectra for both He- and H-implanted surfaces, we conclude that the defects responsible for the 1.86 eV DAP luminescence are passivated by H.

Acknowledgments

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Figure 1. 4.2 K NBE PL of He-implanted (solid line) and unimplanted (dotted line) ZnO. The He-implanted spectrum is scaled by a factor of 20.

Figure 2. 4.2 K PL spectra of (a) He-implanted and (b) unimplanted (0001) ZnO. The sharp peaks near 1.6 eV are the result of second order bound-exciton PL.

Figure 3. Temperature-dependent PL of He-implanted (0001) ZnO. Shown are spectra recorded at: (a) 10 K, (b) 30 K, (c) 50 K, (d) 77 K, and (e) 150 K. Inset: Temperature-dependent normalized total PL intensity (peak intensity times FWHM) of the 1.86 eV peak.

Figure 4. 4.2 K PL of (a) He-implanted and (b) H-implanted (0001) ZnO.

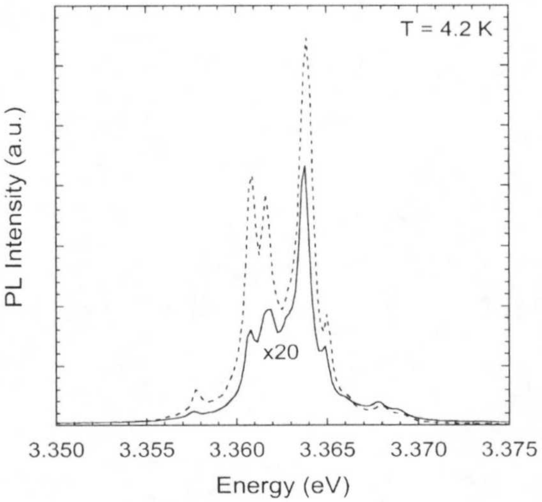

Figure 1. D. W. Hamby, *Nuclear Instruments and Methods in Physics Research - Section B*

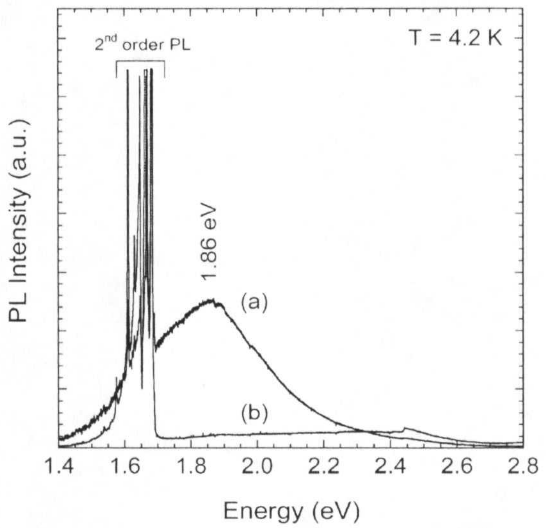

Figure 2. D. W. Hamby, *Nuclear Instruments and Methods in Physics Research - Section B*

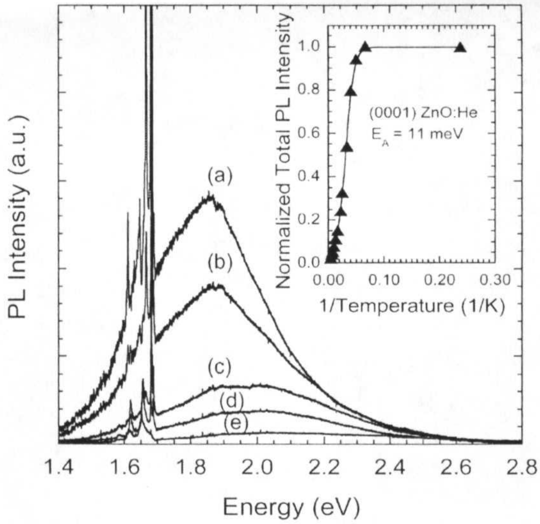

Figure 3. D. W. Hamby, *Nuclear Instruments and Methods in Physics Research - Section B*

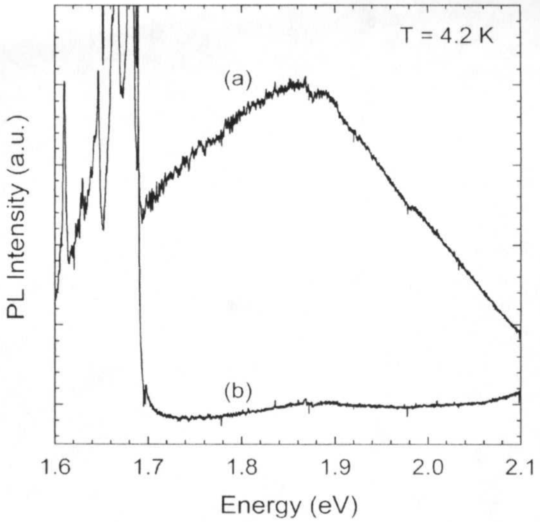

Figure 4. D. W. Hamby, *Nuclear Instruments and Methods in Physics Research - Section B*