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Temperature dependent photoluminescence in oxygen ion implanted and rapid thermally annealed ZnO/ZnMgO multiple quantum wells

Xiaoming Wen[a)]
Centre for Atom Optics and Ultrafast Spectroscopy, Swinburne University of Technology, Melbourne 3122, Australia and Department of Physics, Yunnan University, Kunming, China

Jeffrey A. Davis, Lap Van Dao, and Peter Hannaford
Centre for Atom Optics and Ultrafast Spectroscopy, Swinburne University of Technology, Melbourne 3122, Australia

V. A. Coleman, H. H. Tan, and C. Jagadish
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia

K. Koike, S. Sasa, M. Inoue, and M. Yano
Nanomaterials Microdevices Research Center, Osaka Institute of Technology, Asahi-ku Ohmiya, Osaka 535-8585, Japan

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The authors investigate the effect of oxygen implantation and rapid thermal annealing in ZnO/ZnMgO multiple quantum wells using photoluminescence. A blueshift in the photoluminescence is observed in the implanted samples. For a low implantation dose, a significant increase of activation energy and a slight increase of the photoluminescence efficiency are observed. This is attributed to the suppression of the point defect complexes and transformation between defect structures by implantation and subsequent rapid thermal annealing. A high dose of implantation leads to lattice damage and agglomeration of defects leading to large defect clusters, which result to an increase in nonradiative recombination. © *2007 American Institute of Physics*.
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ZnO is a versatile semiconductor with a large fundamental band gap of ~3.37 eV and an exciton binding energy of 60 meV at room temperature. Together with high thermal conductivity, high luminous efficiency, and mechanical and chemical robustness, ZnO and its alloys have great prospects in optoelectronics applications in the wavelength range from the ultraviolet to the red.[1] Moreover, excitons in ZnO-based quantum well (QW) heterostructures exhibit high stability compared to bulk semiconductors or III-V QWs due to the enhancement of the binding energy and the reduction of the exciton-phonon coupling[2] caused by quantum confinement.

Band gap engineering is an important research field for further ZnO applications. Ion implantation induced intermixing has two main advantages. One is the number of defects introduced by ion irradiation that can be precisely controlled, thus controlling the amount of wavelength shifting, and the other is no further processing and regrowth are required. The point defects induced by ion irradiation usually act as nonradiative centers, which results in a substantial decrease in the photoluminescence (PL) efficiency. Therefore, subsequent rapid thermal annealing (RTA) is performed to remove the remaining defects to recover the optical properties and also to initiate the interdiffusion process. To date many investigations have been performed on the nature of the defects in ZnO and their correlation with the radiative emission bands and nonradiative recombination using various techniques.[3–5] However, the nature of these defects is still not clear and under debate.[2]

In this letter, the effect of oxygen implantation is studied by photoluminescence at low temperature. A significant variation of temperature quenching of photoluminescence intensity is observed, and the mechanism of defect formation after oxygen irradiation and subsequent rapid thermal annealing is proposed.

The sample used in this experiment is a single crystal stack of 19 $ZnO/Zn_{0.7}Mg_{0.3}O$ multiple quantum wells (MQWs) grown on *a*-plane sapphire by molecular beam epitaxy, as reported earlier.[6] The quantum wells are 2 nm thick and the barriers are 5.5 nm thick. After growth, the sample was implanted with 80 keV O^- ions in the dose range of $5\times10^{14}-1\times10^{16}$ cm^{-2} at room temperature, using a 1.7 MV tandem accelerator (NEC, 5SDH-4), followed by rapid thermal annealing at 800 °C in Ar ambient for 60 s, as described by Coleman *et al.*[7] A piece of Si was used to mask a part of the sample during implantation to be used as a reference. The reference and intermixed samples were used in these studies.

The excitation laser pulse used in the photoluminescence experiment is the third harmonic of the fundamental pulses from a Ti:sapphire regenerative amplifier, with a wavelength of 266 nm, pulse duration of 100 fs, and 1 kHz repetition rate. The detector is a UV-visible response photomultiplier tube at the output slit of a 0.25 m monochromator.

A strong near-band edge PL peak is observed for each sample at low temperature, as shown in Fig. 1 for the PL spectra of the implanted sample at 5×10^{14} cm^{-2} (a) and the reference (b). Both samples were annealed at 800 °C for 60 s. This PL band has been studied and mainly attributed to the transitions of the free and bound excitons.[8,9] The implanted samples show an increased blueshift with increasing implantation dose, from a peak of 360 nm for the reference sample to 351 nm for the low ion dose (1×10^{15} cm^{-2}) and

[a)]Electronic mail: xwen@swin.edu.au

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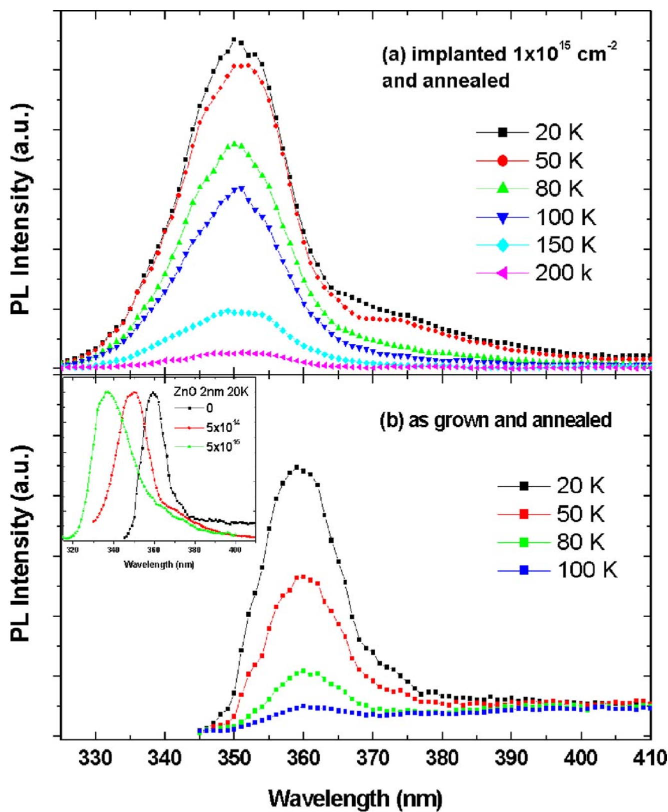

FIG. 1. (Color online) PL spectra at various temperatures for the implanted (a) and as-grown (b) ZnO/ZnMgO multiple quantum well samples. The inset shows an increased blueshift of the PL peak with increasing dose of implantation.

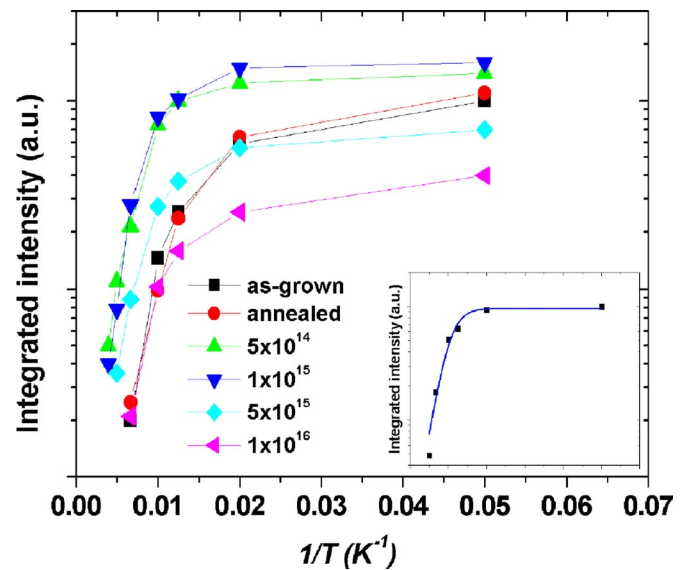

FIG. 2. (Color online) Temperature dependence of the integrated intensity of the excitonic band of ZnO/ZnMgO MQWs. The inset is a fit with Eq. (2) for one of the implanted samples.

336 nm for the high ion dose (1×10^{16} cm^{-2}), as shown in the inset of Fig. 1. At the same time, the ZnO peak becomes broader with increasing ion dose. The reference sample does not show a blueshift, which indicates that RTA does not lead to intermixing. This observation is consistent with the cathodoluminescence experiments by Coleman *et al.*[7]

A remarkable variation of temperature quenching is observed for the reference and implanted samples. With increasing temperature the PL intensity decreases for each sample. In the reference sample, an obvious rapid temperature quenching rate is observed, and the peak intensity decreases to about 10% as the temperature increases from 20 to 100 K. With further increasing temperature, the emission of the quantum wells continuously decreases and is washed out by the emission of the band edge emission of the ZnO bulk at about 200 K. For the implanted sample, on the other hand, a significantly slower temperature quenching rate is observed. The PL intensity remains at more than 50% when the temperature increases from 20 to 100 K and the PL can be observed even at room temperature. The implanted sample with high implantation dose (1×10^{16} cm^{-2}), on the other hand, has a similar quenching rate to the reference sample.

At the same time, the peak intensity is changed by the implantation. At 20 K, the peak intensity of the implanted samples with low dose increases by about 20% compared to the reference sample, while the intensity of the high dose implanted samples decreases significantly relative to the reference.

In order to compare the temperature quenching variation between the reference and implanted samples, an activation energy needs to be introduced to describe the PL quenching process.[10] With optical injection of excitons, the population governing a certain transition is given by

$$\frac{\delta n}{\delta t} = G - \frac{n}{\tau_R} - \frac{n}{\tau_{NR}}, \tag{1}$$

where n is the density of the photoexcited excitons, G is the generation rate, and τ_R and τ_{NR} are radiative and nonradiative lifetimes, respectively. Generally, the exciton PL decay consists of two components, i.e., radiative recombination and nonradiative recombination, with $\tau_{PL}^{-1} = \tau_R^{-1} + \tau_{NR}^{-1}$. The nonradiative recombination rates are thermally activated, whether they correspond to level depopulation or to activation of a nonradiative recombination center, i.e., $\tau_{NR} = \tau_0 \exp(E_a/k_B T)$, where E_a is the activation energy and k_B is Boltzmann's constant.[10] The quantum efficiency can be expressed as $\eta_{PL} = (1 + \tau_R/\tau_{NR})^{-1}$. Thus the nonradiative lifetime τ_{NR} decreases with increasing temperature, which results in a decrease in quantum efficiency and the PL intensity.

The PL intensity is proportional to n/τ_R, and for a quasisteady state, we obtain the familiar expression

$$I = I_0/[1 + \alpha \exp(-E_a/k_B T)], \tag{2}$$

where $\alpha = \tau_R/\tau_0$.

Figure 2 shows an Arrhenius plot of the PL intensity of excitonic bands in the ZnO/ZnMgO MQWs. The inset is a fit with Eq. (2) for a sample with an implantation dose of 1×10^{15} cm^{-2}, which shows that the data are well described by single activation energy. We can deduce the activation energy from Eq. (2), as shown in Fig. 3 (squares). Compared to the reference sample with an activation energy of 17 meV, the implanted samples with low dose irradiation have a significantly larger activation energy of around 30–35 meV. With further increasing the implantation dose, the activation energy decreases to about 20–25 meV, which is still slightly larger than that of the reference sample. Under very high dose (1×10^{16} ions/cm^2), the activation energy decreases to a value of 16 meV similar to the reference. This decrease is due to extensive lattice damage and defect clustering induced

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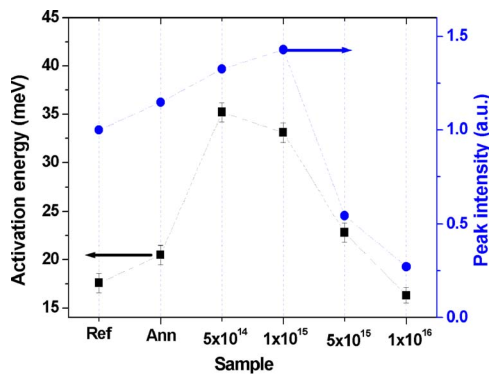

FIG. 3. (Color online) Activation energy (squares) and peak intensity (circles) in 2 nm thick MQW samples. The x coordinate Ref, Ann, 5×10^{14}, 1×10^{15}, 5×10^{15}, and 1×10^{16} represent the sample of the as-grown, RTA, and implanted samples with $5\times10^{14}-1\times10^{16}$ ions/cm^2, respectively.

by the high dose of irradiation, which act as nonradiative centers. The peak intensity variation at 20 K is also shown in this figure (circles), which indicates that the peak intensity is enhanced by low dose implantation. However, high dose ion irradiation results in a decrease in the intensity due to extensive lattice damage and defect agglomeration.

According to the calculation of Kohan *et al.*,[11] the most important factor for determining the concentration of a defect in a crystal is its formation energy E^f which is determined by $C=N_{\text{sites}}\exp(-E^f/k_BT)$, where N_{sites} is the concentration of sites in the crystal where the defect can occur. For ZnO, an oxygen vacancy and zinc vacancy have the lowest formation energy, so they are the most common point defects.[12] It has been shown that dynamic annealing of point defects generated by ion implantation in ZnO is extremely efficient.[13] In the case of oxygen implantation, a myriad of defects can be produced. Recently, Vijayakumar *et al.*[14] reported that the main point defect introduced by oxygen implantation is the zinc vacancy and that a high dose $(2\times10^{16}\ \text{cm}^{-2})$ of irradiation leads to an extensive lattice damage in ZnO sample. At the same time, a marked decrease of carrier mobility is observed in the implanted sample. Due to very effective dynamic annealing and a large mobility of Frenkel pairs in ZnO, most ion implantation induced point defects experience annihilation, and only a small portion of defects survive and form stable defect complexes.[15] Chichibu *et al.*[4] found that certain point defect complexes associated with a zinc vacancy $(V_{\text{Zn}}-X)$ are the dominant nonradiative centers, which result in a reduction of the band edge emission. A single point defect in ZnO, including a zinc vacancy, is unlikely to act as a nonradiative center.

For the implanted sample, the increased PL intensity and the slowed temperature quenching rate suggest that nonradiative recombination decreases in low dose implanted samples. Compared to the reference sample, low dose implantation and subsequent RTA are likely to increase slightly the density of zinc vacancies but they do not act directly as nonradiative centers for the band edge transitions. The most likely situation is that the point defect complexes associated with zinc vacancies or oxygen vacancies[4] are the determining factors for nonradiative recombination.

The activation energy is determined by the detailed structure of the defect complex. It has been suggested that oxygen implantation and subsequent RTA result in a transformation of the defect complexes,[15] creating new defect structures which can have relatively large activation energy. At the same time oxygen implantation leads to significantly poorer carrier mobility, suppressing the formation of the point defect complexes that act as nonradiative centers. Thus the concentration of point defect complexes in the implanted samples is low and an increased PL intensity can be observed. With further increase of the implantation dose, the lattice damage and agglomeration of defects are significantly increased. These defect clusters could again act as nonradiative recombination centers and result in an increase of nonradiative recombination and reduction of PL intensity. However, further work is needed to better understand the mechanism of ion implantation induced defect complexes in ZnO quantum wells.

In conclusion, we have studied the variation of PL quenching as a function of temperature in oxygen ion implanted and rapid thermally annealed ZnO/ZnMgO MQWs. At low doses of ion implantation, the defect complexes, which act as the nonradiative centers, are transformed and suppressed. Thus, oxygen implantation and subsequent RTA cannot only allow band gap engineering for precisely tuning the band gap in a selective area but can also be used to decrease nonradiative recombination, thereby leading to a larger activation energy and a slightly higher PL intensity. A high implantation dose results in extensive lattice damage and large defect clusters, thus resulting in a decrease of the PL intensity and the activation energy.

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