



Effects of annealing temperature on excitonic emissions from Na-implanted ZnO nanorods

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ABSTRACT

The effects of annealing temperature on excitonic emissions from Na⁺ ion implanted ZnO nanorods are studied and annealing between 600 and 800 °C can effectively repair the implantation as evidenced by the enhanced excitonic emissions. A well-resolved bound exciton line at 3.352 eV with a linewidth of ~2 meV emerges from 800 °C annealed sample and could be related to the formation of Na_{Zn} acceptor. When the annealing temperature is increased, the intensity of the I_{6–8} line decreases while that of I₃ increases, suggesting enhanced ionization of neutral donors at elevated temperature.

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1. Introduction

ZnO nanostructures have received much attention due to their unique properties and novel applications [1]. Owing to the asymmetrical doping limitations [2,3], it has been shown to be difficult to obtain high quality and stable *p*-type ZnO which is the key to applications [4]. Considerable efforts have been made to explore the proper *p*-type dopants. The first *p*-type ZnO was reported by Minegishi using N as the acceptor [5]. In 2005, high quality N-doped *p*-type ZnO was realized and room temperature electroluminescence from ZnO *p*-*i*-*n* heterojunction light emitting diode (LED) was demonstrated by Kawasaki's group [6]. Other group-V elements including P [7], As [8] and Sb [9] were also able to produce relatively shallow acceptors in ZnO, although their ionic radii are much larger than that of oxygen. On the other hand, group-I elements such as Li [10], Na [11] and K [12] were also reported to make *p*-type ZnO. Among those dopants, Na has recently gained more attentions. Na has long been regarded as a very deep acceptor [13]. However, recent theoretical and experimental results suggested that it may be a promising acceptor in ZnO and its behaviors should be revisited [11,14–17]. In particular, the optical fingerprint and the energy level of Na acceptor are of fundamental importance but still controversial. The bound exciton recombination at 3.3567 eV (I₉) found in Na-doped ZnO bulk crystal is supposed to be a Na-related acceptor in ZnO [13].

However, later studies indicated that the I₉ line is actually from excitons bound to In-donors [18–20].

ZnO nanostructures are ideal platform for the study of optical properties of acceptors owing to their high crystal quality and easy growth. In this letter, we focus on the low temperature photoluminescence (PL) of Na-implanted ZnO nanorods and the effects of the annealing temperature on the excitonic emissions. The well-resolved excitonic lines allow us to gain an insight into the behaviors of Na acceptor in ZnO. The results suggest that the 3.352 eV emission could be related to the Na acceptor, whose formation strongly depends on the annealing temperature.

2. Experimental details

Vertical ZnO nanorods with diameters ranging from 200 to 500 nm and length of about 8 μm were grown on ZnO seed/*n*-Si substrate using the vapor transport method in a horizontal quartz tube furnace. ZnO (99.99%) and graphite (99.99%) powders were mixed (2:1 by weight) as the source materials. The Si substrate with a ZnO seed layer was placed about 5 cm downstream from the source. Growth of the ZnO nanorods was carried out at 950 °C for 45 min under oxygen and Ar flow ratio of 1:49 at a pressure at 8.5 Torr. Sodium ion implantation was performed at room temperature at 100 kV and the implant fluence was 3.0 × 10¹⁵ cm⁻². After implantation, the samples were annealed in the tube furnace under flowing oxygen for 1 h. The as-implanted sample and samples annealed at 600, 700, 800 and 900 °C were labeled as S1–S5, respectively.

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The surface morphology was characterized by field-emission scanning electron microscopy (FE-SEM) (ULTRA55). The chemical states of Na were determined by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al K_{α} radiation source 1486.6 eV). Low temperature PL measurements were conducted at 13 K on a FLS920 fluorescence spectrometer (Edinburg Instruments) using a He–Cd laser (325 nm) as the excitation source.

3. Results and discussion

The color of the samples changes from black to slight yellow after ion implantation but changes back to black again after annealing. Fig. 1 depicts the SEM top views of the as-grown and Na-implanted nanorods, respectively. The morphology is not changed after ion implantation. According to the Monte Carlo SRIM2003 calculation, the projected range of Na is about 118 nm and the maximum concentration is $1.0 \times 10^{20} \text{ cm}^{-3}$. As shown in Fig. 2, the Na 1s peak centered at 1071.8 eV is detected by XPS from sample S2, confirming that the ZnO nanorods are doped with Na.

Low-temperature (13 K) spectra of the as-implanted and annealed nanorods are exhibited in Fig. 3. Several distinct peaks at 3.357 (I_9), 3.361 (I_{6-8}), 3.367 (I_3) and 3.377 eV (free exciton, FX) are well resolved [18]. The peak at 3.330 eV is known as the Y-line, which has been suggested to be associated with structural defects such as dislocations [21]. The peaks at 3.309 and 3.237 eV are attributed to the longitudinal optical (LO) phonon replica of FX [22], and so are the peaks at 3.289 eV and 3.217 eV of I_9 . The NBE PL intensity of the as-implanted S1 degrades significantly

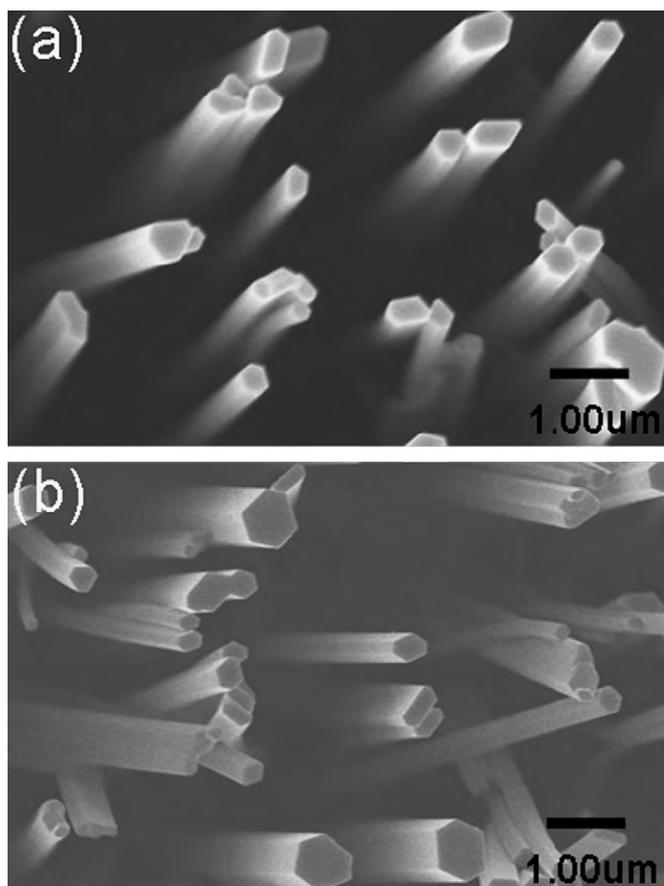


Fig. 1. SEM top views of the ZnO nanorods (a) before and (b) after Na ion implantation.

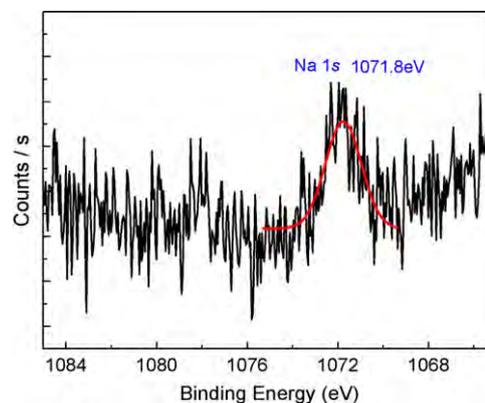


Fig. 2. XPS core level spectra of Na 1s acquired from S2.

due to the radiation damage introduced by ion implantation. After annealing between 600 and 800 °C, the spectra are well resolved and the intensity is greatly enhanced compared to S1. The results indicate that the implantation damage is repaired by annealing. However, if the annealing temperature is increased to 900 °C, the intensity of the NBE emission drops again due to crystal degradation.

Fig. 3(b) shows the magnified PL spectra between 3.33 and 3.39 eV. A new emission line centered at 3.352 eV which is close to I_{10} line [18] is found in S3 and it is more obvious in S4. This line is not observed in S2 and disappears in S5 after annealed at 900 °C. It is noted that positive identification of the I_{10} line is still lacking [18]. Lin et al. [11] and Liu et al. [16] suggest that the peak at 3.352 eV is related to p -type Na dopant in ZnO. Supported by that Na is indeed incorporated into the ZnO nanorods (Fig. 2), the I_{10} line can be assigned to the Na-related acceptor-bound exciton (A^0X). The I_{10} line appears only in S3 and S4 and it can be understood in terms of the formation energy of the Na_{Zn} acceptor and competition between substitutional and interstitial Na atoms. It is suggested that at annealing temperature lower than 800 °C, the formation of Na_{Zn} acceptor is not energetically favorable. At 900 °C, Na may diffuse out from the substitutional sites. Although the doping concentration is as high as $\sim 10^{20} \text{ cm}^{-3}$, the weak I_{10} line indicates that the Na_{Zn} acceptor concentration is rather low even in the sample annealed at 800 °C. The low intensity of the I_{10} line is unlikely due to the presence of deep distorted Na acceptors [23], because no yellow emission at 2.17 eV associated with such deep Na acceptors [15] is observed from our samples.

After annealing, I_{6-8} and I_3 lines emerge in Fig. 3(b). The I_{6-8} line with localization energy of 16 meV corresponds to D^0X and the I_3 line with localization energy separation of 10 meV is believed to stem from the ionized donor bound exciton (D^+X) [18]. Fig. 3(b) shows that the intensity of I_{6-8} line decreases while that of I_3 increases as the annealing temperature is raised to 800 °C, suggesting that a higher annealing temperature increases the number of ionized donors.

4. Conclusion

Low-temperature PL emission from Na^+ ion implanted and annealed ZnO nanorods are studied. The I_{10} line with a narrow linewidth of ~ 2 meV suggests the formation of Na_{Zn} acceptor. At higher annealing temperature, more ionized donors are created as evidenced by that the intensity of I_{6-8} decreases whereas that of I_3 increases. The optimal annealing temperature for the formation of Na acceptor is around 800 °C for Na^+ ion implanted ZnO nanorods.

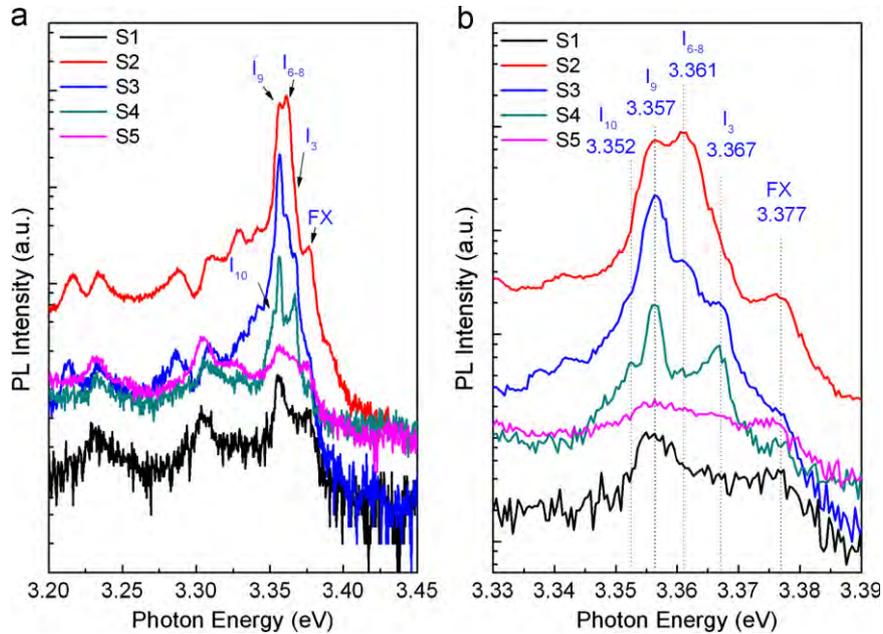


Fig. 3. (a) PL spectra at 13 K acquired from S1–S5. The magnified spectra of (a) in the range of 3.33–3.39 eV are plotted in (b).

Acknowledgments

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