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## Temperature dependent photoluminescence study on phosphorus doped ZnO nanowires

C. X. Shan,<sup>1</sup> Z. Liu,<sup>2</sup> and S. K. Hark<sup>2,a)</sup>

<sup>1</sup>Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

<sup>2</sup>Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, People's Republic of China

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We report temperature dependent photoluminescence studies on phosphorus doped ZnO nanowires. The shape of the spectra is very similar to those of phosphorus doped ZnO films. The photoluminescence spectrum at 10 K is dominated by neutral acceptor bound exciton ( $A^0X$ ) emissions. The acceptor binding energy determined also agrees with the corresponding value in phosphorus doped films. Studies on the  $A^0X$  intensity show two quenching channels, associated with the thermal dissociations of  $A^0X$  to a free exciton and of shallow residual donors. The residual donors revealed provide a clue for the difficulty in  $p$  doping of ZnO. © 2008 American Institute of Physics. [DOI: 10.1063/1.2884312]

Quasi-one-dimensional ZnO nanowires have been studied extensively in recent years for their unique properties and potential applications in acting as building blocks of nanodevices.<sup>1-3</sup> However, since ZnO is usually a  $n$  type semiconducting material, the preparation of durable and reproducible  $p$ -ZnO has long been one of the major hurdles to the applications of ZnO, in nanowire or thin film forms. Many dopants, such as nitrogen,<sup>4</sup> phosphorus,<sup>5</sup> arsenic,<sup>6</sup> and antimony,<sup>7</sup> have been employed to achieve  $p$ -ZnO films. Among them, phosphorus doped ZnO films exhibit high carrier concentrations, reasonable mobility, and low resistivities.<sup>8-11</sup> As for ZnO in the nanowire form, there are very few reports on group-V element doping.<sup>12-17</sup> Lee *et al.* prepared ZnO nanowires by metal organic chemical vapor deposition and thermal evaporation methods on GaAs substrate, then they realized As incorporation into ZnO nanowires by annealing the nanowires.<sup>12,13</sup> Lin *et al.* prepared N doped ZnO nanorods by combining a wet chemical process with post-NH<sub>3</sub> plasma treatment.<sup>14</sup> For phosphorus doped ZnO nanowires, only three reports can be found to the best of our knowledge.<sup>15-17</sup> Hsu *et al.* stated that phosphorus doped ZnO nanowires could be obtained by thermally evaporating mixed powders of Zn and Zn<sub>3</sub>P<sub>2</sub>.<sup>15</sup> Phosphorus doped ZnO nanowires have also been obtained via chemical vapor deposition method employing phosphorus pentoxide as the dopant source.<sup>16</sup> Lee *et al.* prepared MgZnO nanowires, which were then treated with PH<sub>3</sub> plasma; they got phosphorus doped MgZnO nanowires in this way.<sup>17</sup>

Photoluminescence (PL) spectroscopy is a powerful and nondestructive method to explore the characteristics of doped nanowires. Especially temperature dependent PL can reveal the dissociation processes of the impurity bound excitons induced by the doping, and provide useful information for the realization of  $p$ -type ZnO. However, the temperature dependent PL studies on group-V elements doped ZnO nanowires are very scarce.<sup>12,18</sup> As for that on phosphorus doped ZnO nanowires, no report has been addressed to the best of our knowledge.

We have prepared phosphorus doped ZnO nanowires via a simple thermal annealing method.<sup>19</sup> In this letter, the temperature dependent PL characteristics of the phosphorus doped ZnO nanowires are studied. It is found that acceptor bound exciton emission dominates the PL spectrum at 10 K, and its dissociation process is also investigated.

The phosphorus doped ZnO nanowires were obtained by thermal annealing of ZnSe nanowires accompanied by an InP wafer at 700 °C in air ambient. In the process, ZnSe nanowires were converted to ZnO nanowires, while their morphology remained essentially unchanged. Phosphorus that escaped from the InP wafer entered the ZnO nanowires. Consequently, phosphorus doped ZnO nanowires were formed. The detailed preparation conditions can be found in our previous publication.<sup>19</sup> The morphology of the nanowires was characterized by a LEO 1450 scanning electron microscope (SEM). An energy dispersive x-ray detector (EDX) attached to the SEM was used to characterize the composition of the nanowires. The PL studies were carried out from 10 to 296 K, employing the 325 nm line of a He-Cd laser as the excitation source.

The morphology of the nanowires is shown in Fig. 1(a). A high density of woollike nanowires can be observed on the substrate. The average width of the nanowires is about 70 nm, and their length easily exceeds 10 μm. The composition analysis of the nanowires is shown in Fig. 1(b). Besides the peak from the Si substrate, peaks from Zn, O, and P can also be observed in the EDX spectrum, revealing the incorporation of phosphorus into the ZnO nanowires.

The temperature dependent PL spectra of the phosphorus doped ZnO nanowires are shown in Fig. 2. The 10 K spectrum can be well fitted by six Gaussian peaks, and the dominant sharp peak is located at 3.353 eV, with a full width at half maximum of 8.9 meV. The position of this peak accords well with the neutral acceptor bound exciton ( $A^0X$ ) emission in ZnO.<sup>20</sup> This peak is also observed in phosphorus doped ZnO films<sup>8,11</sup> and nanowires.<sup>16</sup> Therefore, it is attributed to the  $A^0X$  emission. Just like what was observed in phosphorus doped ZnO,<sup>8,11,16</sup> the 10 K PL spectrum of the doped ZnO nanowires in our case is dominated by  $A^0X$ . The shape of the spectrum is almost identical to that of phosphorus doped  $p$ -ZnO films.<sup>8</sup> The similarity between the PL spectra

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: skhark@phy.cuhk.edu.hk.

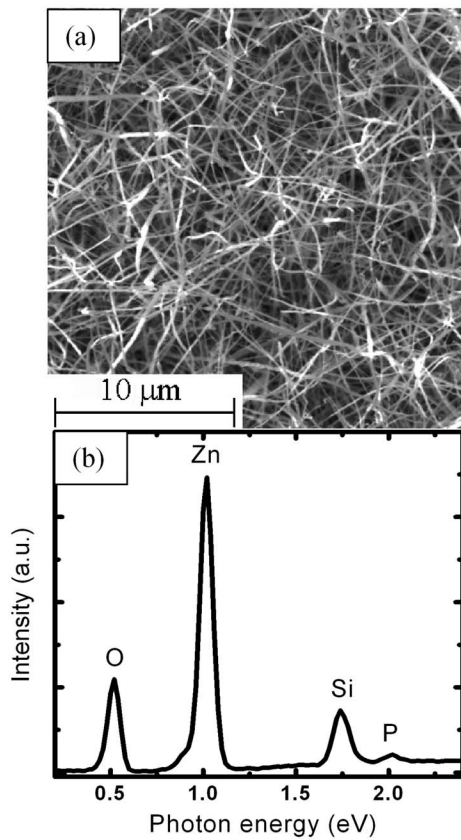


FIG. 1. (a) Typical SEM image of the phosphorus doped ZnO nanowires; (b) EDX spectrum of the nanowires, revealing the incorporation of phosphorus.

of our samples and those of previous reports provide additional support to the occurrence of doping in the nanowires. There appear two other peaks at 3.315 and 3.296 eV. With increasing temperature, the latter diminishes very quickly and its peak position blueshifts slightly, meanwhile, the former becomes dominant gradually, which are typical features of donor-acceptor pair (DAP) emission.<sup>21</sup> Therefore, the 3.296 eV peak is attributed to the DAP emission, and the 3.315 eV peak to the conduction-band-to-acceptor ( $eA^0$ ) transition. As the donor bound excitons dissociate gradually, emission from the free electrons to acceptor bound holes becomes dominant with increasing temperature. A broad weak peak is also observed at 3.245 eV. Since its energy difference with the  $eA^0$  peak (70 meV) is almost identical to the phonon energy in ZnO (72 meV), it can be attributed to the phonon replica. It is noted that there appears a shoulder at about 3.370 eV, and its position is close to the reported  $A$ -exciton emission (3.372 eV at 10 K).<sup>16</sup> Moreover, it gradually becomes more prominent with increasing temperature. Therefore, the shoulder is attributed to the free exciton emission ( $X_A$ ) in ZnO. For comparison, the PL spectrum of undoped ZnO nanowires taken at 20 K is displayed in the inset of Fig. 2(a). There appear three main peaks as well as one weak shoulder at 3.249, 3.318, 3.356, and 3.370 eV, respectively. As described previously, the shoulder at 3.370 eV comes from the free exciton emission in ZnO.<sup>16</sup> The position of the peak at 3.356 eV is very close to that of the donor-related signals [3.358 eV (Ref. 22)], therefore, it is tentatively labeled as  $SD_2$  after Ref. 22. The 3.318 eV peak is from the emission of another donor-acceptor pair,<sup>21</sup> and is marked DAP1. The peak at 3.249 eV has an energy 69 meV

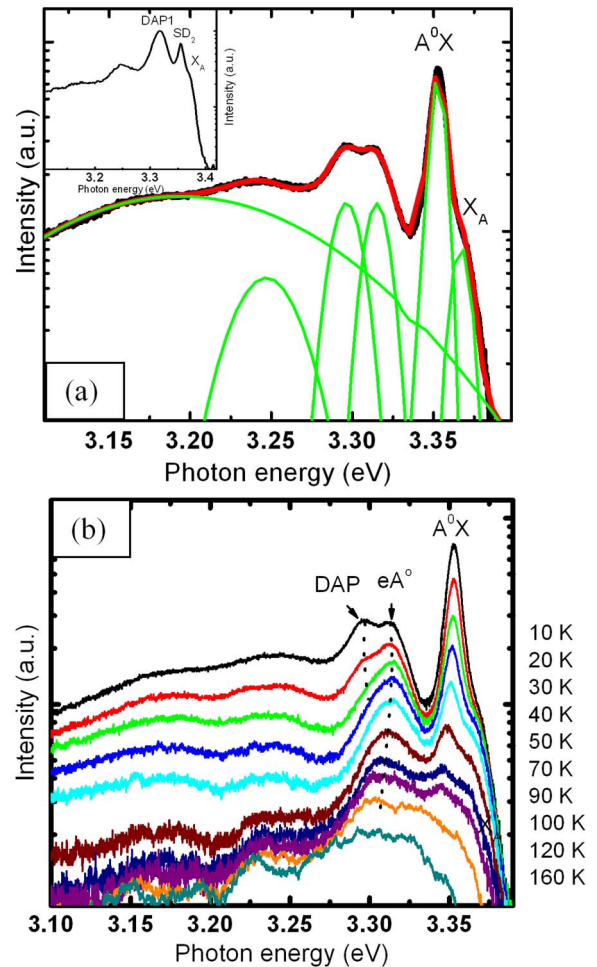


FIG. 2. (Color online) (a) PL spectrum of phosphorus doped ZnO nanowires at 10 K, it can be well fitted by six Gaussian peaks, and the inset shows the PL spectrum of undoped ZnO nanowires taken at 20 K for comparison; (b) temperature dependent PL spectra of the phosphorus doped ZnO nanowires.

lower than DAP1, which is close to the phonon energy in ZnO; therefore, it is attributed to the phonon replica of DAP1. The prominent  $A^0X$  emission in the PL spectrum of doped ZnO nanowires in comparison to that of undoped ones suggests the incorporation of acceptors.

The acceptor binding energy of  $E_A$  in ZnO can be estimated by the following formula:<sup>23</sup>

$$E_A = E_{\text{gap}} - E_{FA} + k_B T / 2, \quad (1)$$

where  $E_{FA}$  is the transition energy of  $eA^0$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. With an intrinsic band gap of  $E_{\text{gap}} = 3.437$  eV,<sup>23,24</sup> the acceptor binding energy of  $E_A$  can then be calculated to be about 182 meV, considering the 60 meV exciton binding energy of ZnO. It is noteworthy that the  $E_A$  value we obtained from Eq. (1) is also almost identical to that reported by Xiu *et al.* (180 meV) in phosphorus doped  $p$ -ZnO films.<sup>9</sup>

The temperature dependent  $A^0X$  emission intensity of the phosphorus doped ZnO nanowires is shown in Fig. 3, in which rectangles show experimental data and the curves present fitted results using the following formula:<sup>25</sup>

$$I(T) = \frac{I_0}{1 + C_1 \exp(-E_1/K_B T) + C_2 \exp(-E_2/K_B T)}, \quad (2)$$

where  $I(T)$  and  $I_0$  are the PL intensities at temperature  $T$  and 0 K, respectively.  $C_1$  and  $C_2$  are constants, and  $E_1$  and  $E_2$  are



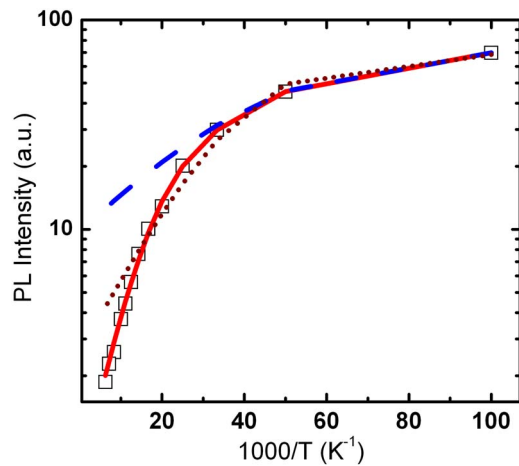


FIG. 3. (Color online) Variation of the intensity of the  $A^0X$  emission with inverse temperature, in which the scattered rectangles are experimental data; the dotted line is the best fitting result considering only one quenching channel; the solid line is the best fitting result considering two quenching channels; and the dashed line is the calculated result by ignoring the first quenching channel while keeping other parameters fixed.

dissociation energies. By making  $C_2$  zero in Eq. (2), namely, considering that there is only a single channel contributing to the quenching of the  $A^0X$  with temperature, the best fit result is shown by the dotted curve in Fig. 3. The huge discrepancy reveals that the experimental data can not be well fitted this way, which suggests to us that there may be another quenching channel. By taking two quenching channels, the experimental data can be fitted very well, as shown by the solid line in Fig. 3. The two-channel fitting yields  $C_1=6.5$ ,  $C_2=110.4$ ,  $E_1=4.1$  meV, and  $E_2=17.7$  meV. It is noted that  $E_2$  almost equals to the energy separation between  $A^0X$  and  $X_A$  (17 meV), which implies to us that the second quenching channel may be the thermal dissociation of the neutral acceptor bound exciton to a free exciton. To explore the origin of the other quenching channel, we set  $C_2$  to zero while keep the values of  $I_0$ ,  $C_1$ , and  $E_1$  in Eq. (2), then the dashed line in Fig. 3 is obtained. As shown, the dashed line fits the experimental data very well at very low temperatures; while at about 40 K and above, the calculated data deviate from the experimental results gradually. Note that the thermal energy at 40 K corresponds to 3.5 meV, which is close to  $E_1$ . By studying the temperature dependent spectra of DAP emission shown in Fig. 2(b), one can find that the DAP peak totally merge into the  $eA^0$  at about 40 K. It is accepted that thermal dissociation of the donors will lead to the diminishing of the DAP emission, while enhancing of the  $eA^0$  emission. Therefore, it is presumed that the first quenching channel might come from the thermal dissociation of neutral residual donors. In fact, there is really a bound exciton line known as  $I_1$  with the dissociation energy of 4.1 meV in ZnO.<sup>26</sup> This emission is interpreted to come from the donor bound exciton recombination, likely induced by residual impurity.<sup>22</sup> The sharp agreement between the dissociation energy of  $I_1$  and  $E_1$  supports that the first quenching channel come from the thermal dissociation of residual donor.

In conclusion, temperature dependent photoluminescence of phosphorus doped ZnO nanowires has been investigated. The 10 K PL spectrum was dominated by the acceptor bound exciton emission, induced by the phosphorus doping. The shape of the PL spectra is very similar to that of phosphorus doped ZnO films. The acceptor binding energy

obtained also accords well with the value reported in phosphorus doped ZnO films. Temperature dependent studies on  $A^0X$  emission reveal that there are two quenching channels, one is the thermal dissociation of residual donors in ZnO with a dissociation energy of 4.1 meV, and the other is the dissociation of acceptors induced by phosphorus doping with a dissociation energy of about 17.7 meV. The very shallow background donors (with dissociation energy of 4.1 meV) revealed in this study may provide a clue for the huge difficulties in obtaining stable and reproducible  $p$ -ZnO. It is expected that  $p$ -ZnO could be attainable if the shallow donors could be reduced.

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