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Nitrogen deep accepters in ZnO nanowires induced by ammonia plasma

Rui Huang,[1,2] Shuigang Xu,[1] Wenhao Guo,[1] Lin Wang,[1] Jie Song,[2] Tsz-Wai Ng,[3] Jianan Huang,[3] Shuit-Tong Lee,[3] Shengwang Du,[1] and Ning Wang[1,a)]
[1]*Department of Physics and the William Mong Institute of Nano Science and Technology, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR*
[2]*Department of Physics and Electronic Engineering, Hanshan Normal University, Chaozhou, Guangdong, China*
[3]*Department of Physics and Materials Science, City University of Hong Kong, Kowloon Tong, Hong Kong SAR*

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Nitrogen doping in ZnO nanowires was achieved through ammonia plasma treatment followed by thermal annealing. The strong dependence of the red light emission from the nanowires excited by 2.4 eV on the nitrogen concentration, suggests that the red light emission originates from nitrogen related defects. The mechanism responsible for the red light emission is in good agreement with the deep-acceptor model of nitrogen defects, clarifying that nitrogen atoms caused deep accepters in ZnO nanowires. Based on this model, the enhanced green emission from defects in nitrogen-doped samples (excited by 325 nm line) can be well explained by the increase of the concentration of activated oxygen vacancies resulting from the compensation of nitrogen deep acceptors. © *2011 American Institute of Physics*. [doi:10.1063/1.3647773]

In the past decade, one-dimensional ZnO nanostructures have aroused great research interests owing to their wide direct bandgap and large exciton binding energy. Up to now, their excellent optical and electrical properties have been reported widely, and the performance of ZnO-based devices has been improved significantly.[1–5] However, there is still a long way towards the realization of practical ZnO-based optoelectronic devices. The main obstacle lies in the lack of reliable p-type doping in ZnO. In fact, many sophisticated strategies have been employed to achieve suitable p-type doping in ZnO.[5–13] Among them, nitrogen has been considered as a promising p-type dopant of ZnO because of its similar ionic radius to oxygen.[14] Although nitrogen incorporation in ZnO has been intensively investigated experimentally and theoretically, the progress along this direction is slow, and nitrogen doping mechanisms and modes[15–19] are still controversial.

According to previous experimental and theoretical works, nitrogen is usually considered as a shallow acceptor in ZnO.[16,17] Lyons *et al*. demonstrated that nitrogen deep acceptors showed an acceptor level of 1.3 eV above the valence band maximum,[18] which was also supported by recent experimental results of Tarun *et al*.[19] In this letter, we provide evidences that nitrogen shows deep accepter characteristics in ZnO nanowires. By correlating nitrogen concentration and evolution of red light emission, we suggest that the enhanced defect green emission in the nitrogen-doped samples is due to compensation of oxygen vacancies by nitrogen deep accepters.

ZnO nanowires were prepared by the chemical vapor transport method on silicon substrates as reported elsewhere.[20] To achieve nitrogen doping in ZnO nanowires as well as to passivate defect states, NH_3 plasma irradiation was subsequently carried out using plasma-enhanced chemical vapor deposition at high frequency (40.68 MHz). The plasma power density was 1.2 W/cm^2 and the deposition was carried out at 350 °C. To activate nitrogen dopants and control dopant concentration, samples were post-annealed in a N_2 atmosphere at different temperatures. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of nitrogen dopants in the samples. The structure of nanowires was characterized by a Philips XL30 scanning electron microscope (SEM). The excitation sources for the photoluminescence (PL) investigation of ZnO nanowires were He-Cd (325 nm) and Ar ion (516 nm) lasers.

Fig. 1(a) shows the PL spectra of the ZnO nanowires treated by NH_3 plasma for different durations. The PL spectrum taken from the as-deposited sample exhibits two emission bands. One is the UV band with a peak position at 378 nm, caused by the excitonic recombination, and the other is the green band, which is commonly regarded as the deep-level defect emission (DE) caused by the oxygen vacancies.[21] For the NH_3 plasma-treated ZnO nanowires, one can see that the green emission has been completely eliminated, while the UV emission is two times higher than that from the ZnO nanowires without NH_3 plasma treatment. The elimination of the green emission by NH_3-plasma surface treatment indicates that the deep-level defects such as oxygen vacancies should mainly come from the nanowire surfaces. On the other hand, the obvious nitrogen peak in the XPS spectrum shown in Fig. 1(b) demonstrates the existence of nitrogen atoms in ZnO nanowires. It is well known that nitrogen (or hydrogen) atoms can effectively passivate surface defect states.[22,23] The typical SEM image shown in the inset of Fig. 1(a) reveals that the morphology of the ZnO nanowires remains intact even after 30 min NH_3-plasma treatment.

To activate nitrogen acceptors in the nanowires, the samples were post-annealed at various temperatures up to 800 °C in a N_2 atmosphere. As shown in Fig. 2(a), the PL spectra excited by 2.4 eV were analyzed to identify the nitrogen accepter states in ZnO nanowires.[18] A strong emission

a)Author to whom correspondence should be addressed. Electronic mail: phwang@ust.hk.

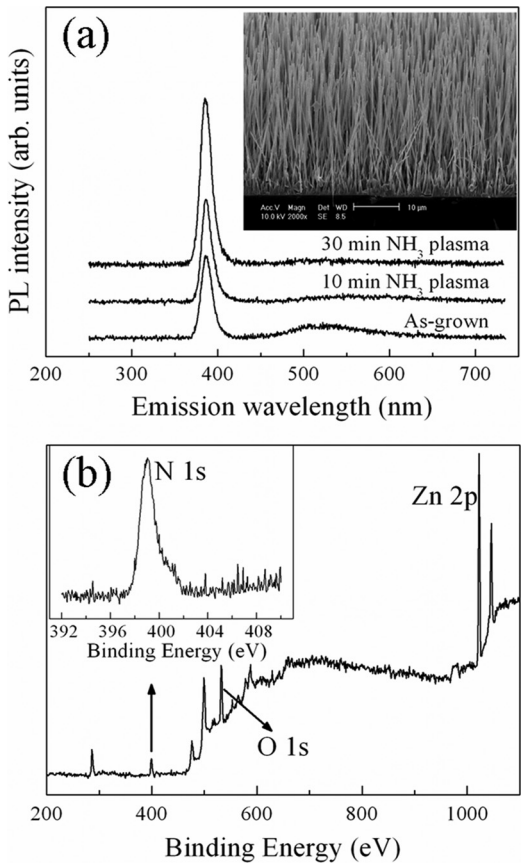

FIG. 1. (a) PL spectra of the ZnO nanowires treated by NH_3 plasma for different duration. The inset shows the SEM image of the sample treated by NH_3 plasma for 30 min. (b) XPS data of the sample treated by NH_3 plasma for 30 min. The inset shows N 1 s spectrum of the corresponding sample.

band centered at 730 nm is clearly visible in the sample annealed at 400 °C. With annealing temperature increased to 500 °C, the intensity of this emission band rapidly decreases and the broad band develops into two pronounced peaks at 730 nm and around 600 nm, respectively. The PL band at 600 nm, commonly referred to as the oxygen-related defect

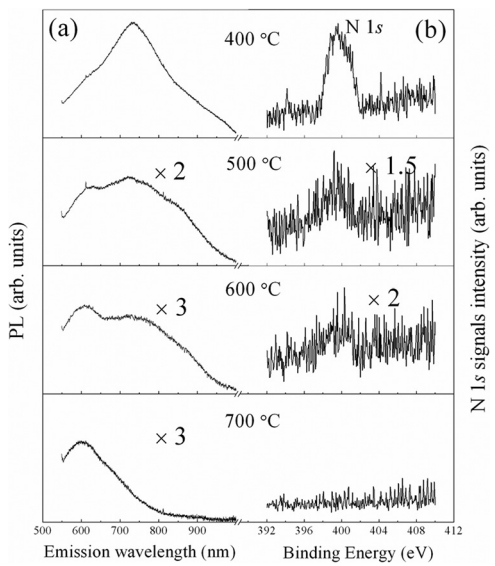

FIG. 2. (a) PL spectra and (b) XPS spectra of the N-doping samples annealed at various temperatures. He-Cd and Ar ion lasers were used as the excitation sources to obtain the PL spectra.

emission, does not appreciably change even though the annealing temperature is increased up to 800 °C. In contrast, the 730 nm PL band is highly sensitive to the annealing temperature and can be completely eliminated at 700 °C.

To explore the origin of the red emission, we carefully examine the chemical states of the nitrogen dopants in the samples. Figure 2(b) displays the evolution of N 1 s XPS spectra for the samples treated with different annealing temperatures. The N 1 s signals are clearly visible for the samples annealed below 600 °C, although the intensity of the signals becomes much weaker for the sample annealed at 600 °C, presenting a direct evidence for the existence of nitrogen in the samples. The rapid decrease in N 1 s signal intensity with increasing annealing temperature indicates a significant reduction of nitrogen content in the samples. The nitrogen signal disappears when the annealing temperature is higher than 700 °C. We believe that nitrogen dopants have been desorbed from the sample at such a high annealing temperature. We note that decreasing red emission intensity with increasing annealing temperature exhibits a similar trend to the change of the nitrogen content in the samples. Therefore, the decrease of red emission intensity can be ascribed to the decrease of nitrogen concentration, or the red light emission is due to the nitrogen related defects. According to density function calculations, Lyons *et al*. showed that nitrogen can act as deep acceptors and cause significant crystal lattice relaxation.[18] In the deep-acceptor model, the energy of optical absorption and emission is estimated to be 2.4 eV and 1.7 eV, respectively, according to the configuration coordinate diagram.[18] Apparently, in the present samples, the red light emission band at ~1.7 eV generated by 2.4 eV excitation is in good agreement with the deep-acceptor model of nitrogen defects. This further suggests that nitrogen acts as deep accepters in ZnO nanowires.

The 325 nm line of He-Cd laser was also used to investigate the PL properties in the samples with and without nitrogen doping. The normalized PL spectra are displayed in Fig. 3. The green emission from defects appears in all samples. As shown in the inset in Fig. 3, it is interesting to find that the ratio of the integrated intensity of the DE to the UV emission (near-band-edge emission, NBE) is always higher in the nitrogen-doped ZnO nanowire samples than that in the undoped samples for the same annealing temperature. The origin of the green emission is generally assigned to the

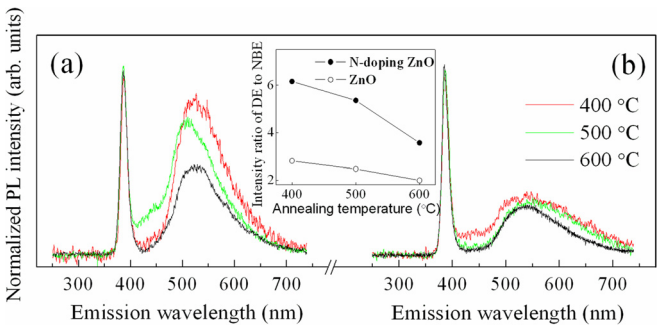

FIG. 3. (Color online) The normalized PL spectra of the samples (a) with and (b) without nitrogen doping, respectively, which were excited by the 325 nm line of He-Cd laser. The inset shows the intensity ratio of the DE to the UV emission (NBE) of the samples with and without nitrogen doping, respectively.

single positively charged oxygen vacancies (V_o^+). These vacancies need to be activated by trapping holes.[21] In the nitrogen-doped ZnO samples, since the energy level of the nitrogen acceptors (1.3 eV above the valence band maximum) is slightly higher than that of oxygen vacancies (V_o^+),[18] the holes would transfer from the nitrogen acceptor level to the V_o^+ level, contributing to the formation of activated oxygen vacancy (V_o^{++}). The increase of V_o^{++} concentration undoubtedly results in a higher intensity ratio of the defect emission to the UV emission in the nitrogen-doped ZnO samples as compared to the undoped samples. These results also indicate that the unintentional n-type doping effect in ZnO induced by oxygen vacancies can be balanced out by the nitrogen deep acceptors. Therefore, a dual-acceptor dopant (nitrogen as one component) can form through the NH_3 plasma treatment, which is expected to provide a feasible route to obtain stable and reproducible p-type doping in ZnO nanowires. Recently, Sun *et al*. reported that reproducible p-type doping of ZnO films was realized by employing Li-N as a dual-acceptor dopant.[24] Their results are consistent with our model and prediction.

In summary, we demonstrate that nitrogen can be induced into ZnO nanowires as deep accepters by NH_3 plasma treatment followed by thermal annealing. Based on the deep-acceptor model of nitrogen defects, the enhanced green emission in nitrogen-doped samples was explained by the increase of activated oxygen vacancies resulting from compensation of nitrogen deep acceptors. The unintentional n-type doping effect in ZnO induced by oxygen vacancies can be balanced out by nitrogen deep acceptors. By forming dual-acceptor dopants, NH_3 plasma treatment is expected to provide a feasible route to obtain stable and reproducible p-type doping in ZnO nanowires.

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