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Citation: Appl. Phys. Lett. **98**, 062102 (2011); doi: 10.1063/1.3549304
View online: http://dx.doi.org/10.1063/1.3549304
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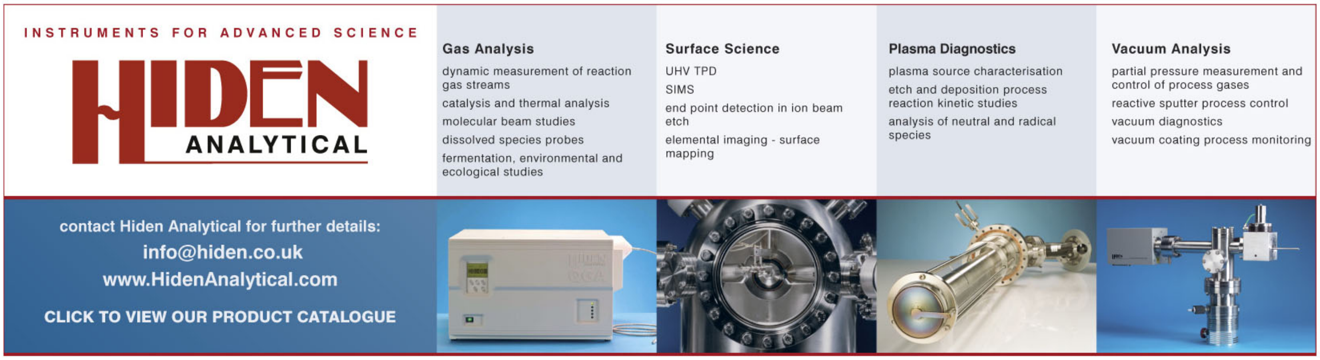

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APPLIED PHYSICS LETTERS **98**, 062102 (2011)

The p-type ZnO film realized by a hydrothermal treatment method

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(Received 25 November 2010; accepted 3 January 2011; published online 7 February 2011)

Reproducible and high quality N-doped ZnO (ZnO:N) films were achieved by a hydrothermal treatment method. The ZnO:N films exhibited p-type characteristics by means of the Hall-effect and the photoluminescence measurements. At room temperature, the electrical properties of ZnO:N film showed a hole concentration of 1×10^{16} cm^{-3} and hole mobility of 8.6 cm^2 V^{-1} s^{-1}. At 83 K two acceptor related emission peaks could be observed located at 3.353 and 3.237 eV, which were assigned to the acceptor-bound exciton and the donor-acceptor pair emissions. This result gave a direct evidence for the generation of the acceptor energy level after the hydrothermal treatment process. Also, a ZnO homojunction diode was fabricated by this method, which displayed a good rectification characteristic at room temperature. This study revealed that the hydrothermal treatment method was effective and practicable in producing p-type ZnO. © *2011 American Institute of Physics*. [doi:10.1063/1.3549304]

ZnO is a direct wide band gap semiconductor and has a larger exciton binding energy of 60 meV, which is 2.4 times larger than that of GaN (21 meV). This indicates that ZnO should be a potential material to realize high efficient excitonic ultraviolet (UV) optoelectronic devices, such as UV light-emitting diodes and laser diodes,[1,2] and so on.

Because of the native defect, such as zinc interstitials and oxygen vacancies,[3–5] ZnO usually presents n-type conductivity. There are several problems to limit the efficient p-type doping in ZnO including the low dopant solubility, the deep acceptor level, and the "self-compensation" of shallow acceptors resulting from native donor defects,[6] which hinder the development of the efficient ZnO based optoelectronic devices. To overcome these problems, many growth techniques and the post-treatment methods were employed to fabricate the p-type ZnO with different dopants.[7–10] Group-I elements (Li, Na,) and group-V elements (N, P, As, Sb) were tried as the suitable dopants to realize the p-type conductivity in ZnO. By now, although there have been lots of reports about the fabrication and characterization of p-ZnO and ZnO p-n homojunctions, it is still very difficult to achieve a reliable and reproducible p-type ZnO film.

In this paper, a post-treatment method was carried out to obtain a nitrogen doped p-type ZnO thin film. For the traditional post-treatment process a high temperature was needed to promote the diffusion for the dopants, which could induce the roughness of the film surface.[11] Considering this point and to reduce the escape rate of the dopants, a hydrothermal method was used in the treatment process. In this process the low temperature would keep the surface morphology unchanged and the high pressure would promote the diffusion and reduce the escape rate for the dopants. To date, there has been no report about the hydrothermal treatment to realize a p-type doping ZnO film.

The undoped ZnO film was grown on a c-plane Al_2O_3 substrate using the plasma-assisted molecular beam epitaxy technique. The growth details were described in our previous publication.[7] The as-grown ZnO film had a thickness of about 300 nm and showed n-type conduction with an electron concentration of $3 \times 10^{16}/\text{cm}^3$ and an electron mobility of 33 cm^2 V^{-1} S^{-1}.

The as-synthesized sample was cut into four pieces for the following treatment via the hydrothermal method. The aqueous solution containing 10 mM hexamethylenetetramine (HMT) was transferred to a Teflon-lined stainless autoclave. The reaction temperature was kept at 90 °C, and the reaction time was 18, 24, and 48 h, respectively. After the autoclave was cooled to room temperature, the samples were taken out of the solution and washed by de-ionized water several times. Subsequently, samples were dried in an oven at 60 °C for 24 h. Finally, samples were annealed at 450 °C for 5 min in air. The as-synthesized sample and samples treated for 18, 24, and 48 h were labeled as samples A, B, C, and D, respectively. To make a homojunction diode, n-ZnO layer with the thickness of 200 nm was capped on a part of sample B using an electron beam evaporation method at 400 °C. Meanwhile, Au–Ni and In electrodes were used to form Ohmic contact to the p-type and the n-type layers, respectively

To explore the electrical properties of the thin films, a van der Pauw method was performed at room temperature. The electrical properties of the films were measured with a Hall measurement system (LakeShore 7707) at room temperature. The measurement data are displayed in Table I. The results show that the as-grown film is n-type conduction with an electron concentration of $3 \times 10^{16}/\text{cm}^3$ and an electron mobility of 33 cm^2 V^{-1} S^{-1}. But after the treatment, the electrical conduction type turns from n-type to p-type. The electrical properties of the treated ZnO film show the hole concentration in the range of 1×10^{16} cm^{-3} and the maximum hole mobility of 8.6 cm^2 V^{-1} s^{-1} (sample B).

Because of the photoluminescence (PL) emission are sensitive to the defect states in semiconductors, the PL mea-

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TABLE I. Electrical properties of ZnO and ZnO:N films measured by van der Pauw method at room temperature.

Sample	Carrier type	Carrier density (cm^{-3})	Mobility ($cm^2\ V^{-1}\ s^{-1}$)
A	n	3×10^{17}	3.3
B	p	1×10^{16}	8.6
C	p	4.4×10^{16}	0.8
D	p	2.2×10^{15}	4

surement was carried out with a JY-630 micro-Raman spectrometer by using the 325 nm line of a He–Cd laser as the excitation source. To further understand the effect of the treatment, the low-temperature PL measurement was performed at 83 K, as shown in Fig. 1. For the as-grown ZnO film, the spectrum is mainly dominated by the free exciton (FX) located at 3.375 eV and the shallow donor-bound exciton (D^0X) at 3.361 eV. The emission peaks located at 3.316 and 3.246 eV are considered as the 1-LO (longitudinal optical) and 2-LO phonon replicas of free exciton, respectively. Compared with the PL spectrum of the pure ZnO and the treated ZnO films, the difference between them is evident. The low-temperature PL spectrum of sample B consists of four main emission bands located at 3.353, 3.312, 3.237, and 3.168 eV, respectively. The emission peak located at 3.353 eV could be ascribed to the acceptor-bound exciton radiative recombination (A^0X). Another peak located at 3.312 eV is usually assigned to the transition of the free electron from conduction to acceptor level (FA) related to the nitrogen acceptor, which is in accordance with the previous reported experimental data in N-doped ZnO thin film.[12] Previously, the FA emission peak around 3.310 eV also appeared in P-doped[13] and As-doped ZnO.[14] Moreover, the emission peak located at 3.237 eV is attributed to the donor-acceptor pair (DAP) transition. The emission peak at 3.168 eV, which is 69 meV lower in energy than DAP, is assigned to the 1-LO phonon replica of DAP because the difference value between them is in agreement with the longitudinal optical phonon energy of ZnO.

In order to further investigate the acceptor related emissions, the temperature-dependent PL spectra were studied (as shown in Fig. 2). Because of the thermal dissociation, the emission intensity of A^0X decreases quickly and almost disappears at 115 K. For the FA and DAP emissions, both peaks could be detected at high temperature with the peak position shifting to the low energy side. At room temperature a mixed emission containing FX and FA is dominant in the spectrum.

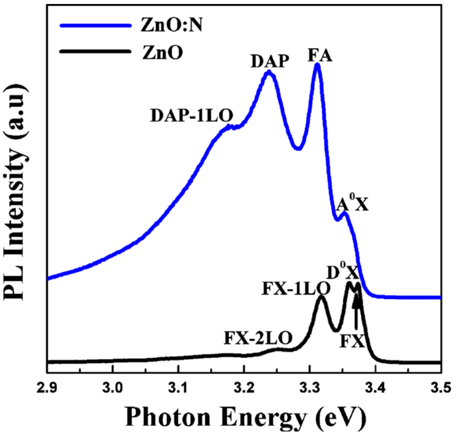

FIG. 1. (Color online) PL spectra of as-grown ZnO film (sample A) and p-type ZnO:N film (sample B) at 83 K.

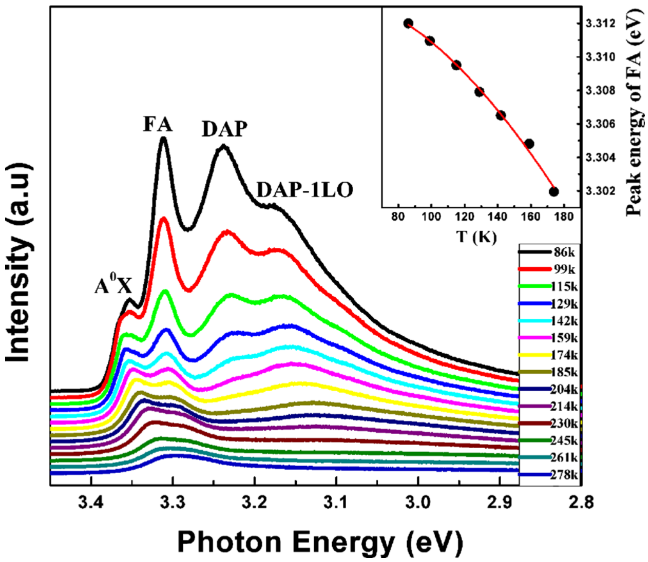

FIG. 2. (Color online) The temperature-dependent PL spectra of the ZnO:N film (sample B). The inset shows the temperature-dependent peak energy of FA and the fitting curve using Eq. (1) for sample B.

The temperature-dependent peak position of the FA emission is shown in the inset of Fig. 2. It can be seen that the FA transition energy shows a continuous red-shift with increasing temperature. The acceptor binding energy of E_A in ZnO could be estimated by the following equation:

$$E_{FA}(T) = Eg(T) - E_A + \tfrac{1}{2}K_BT, \qquad (1)$$

where Eg(T) and $E_{FA}(T)$ are the temperature-dependent band gap energy and free electron to acceptor energy, respectively. K_B is the Boltzmann constant. Here, Eg(T) is a function of temperature, which is fitted well with the formula $Eg(T) = Eg(0) - \alpha T^2/(\beta + T)$, where α and β are constants. Eg(0) is the band gap energy at T=0 K. Based on the above equations, the acceptor energy level could be calculated to be about 112 meV, which is in good agreement with those reported by Sun *et al.*[15]

In the experiment, HMT is acted as dopant source. HMT could hydrolyze at high temperature through the following equations:

$$(CH_2)_6N_4 + 10H_2O \leftrightarrow 6HCHO + 4NH_3 \cdot H_2O, \qquad (2)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-, \qquad (3)$$

$$NH_3 \rightarrow (NH)^{2-} + 2H^+. \qquad (4)$$

ZnO has a wurtzite structure with low symmetry, which is described as many planes that constitute fourfold coordinated O^{2-} and Zn^{2+} ions stacked along the c axis, resulting in the existence of spontaneous polarization along the (0001) direction.[16] For the basal planes, the (0001) plane is terminated by Zn ions. Because the Zn ions have positive charges, it will attract the OH^- due to the Coulomb force, forming a very little $Zn(OH)_2$ on the surface of ZnO film. $Zn(OH)_2$ dehydrated can change into ZnO after drying. The raised parts on the ZnO thin film have higher chemical reaction activity, due to this reason the surface of the thin film tends to smooth after the hydrothermal treatment.[17] As described

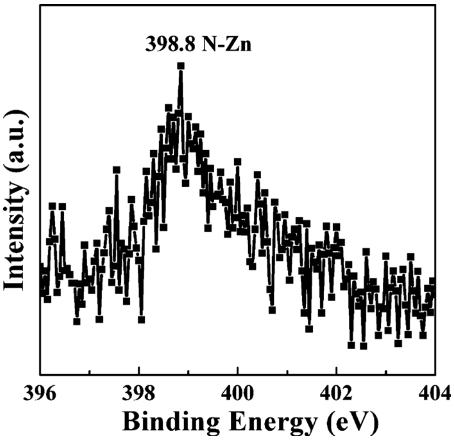

FIG. 3. XPS of sample B.

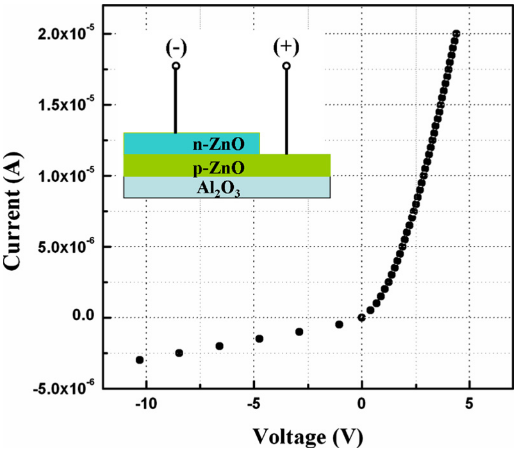

FIG. 4. (Color online) The I-V characteristics of the ZnO homojunction at room temperature. The inset is the schematic structure of the ZnO p-n junction.

above, this treatment method contains the doping and etching processes, and the interfaces property between different grains could be affected during these processes, which is a very important factor to the measured Hall mobility. Due to the change of the interface properties the mobility presents the irregular variety under different treated conditions.

Meanwhile, during the treatment progress the generated ammonium complex compound could be used as N sources, which could coordinate with Zn ions. The above reactions are considered a chemical etching and coordination process, which leads to the nitrogen doped into the ZnO thin film efficiently. Also, the high pressure generated in the hydrothermal process would promote the N atoms doping in ZnO. Figure 3 shows the x-ray photon electron spectroscopy (XPS) of sample B. A weak photon emission peak located at 398.8 eV was detected. Based on the previous report, this value was ascribed to the nitrogen signal from the N–Zn bond.[7] The XPS datum indicates that the nitrogen atoms could substitute O position in ZnO thin film after the hydrothermal treatment, which is the origin of the p-type doping for the treated ZnO.

To verify the p-type conduction of the treated samples, an undoped n-ZnO layer was deposited on the surface of the treated ZnO thin film to form a ZnO homojunction diode (the schematic structure of the ZnO p-n junction is shown in the inset of Fig. 4), and the current-voltage (I-V) measurement was performed at room temperature. As shown in Fig. 4, the I-V curve of the diode displays a good rectification characteristic with a threshold voltage of 2 V at forward bias at room temperature. This result could be considered as a proof of the p-type behavior for the treated sample achieved by the hydrothermal method.

In summary, p-type ZnO thin film was achieved via a hydrothermal treatment processing. It was believed that the high pressure generated at the hydrothermal process would promote the p-type doping in ZnO. By the measurements of the van der Pauw method and the low-temperature photoluminescence, the p-type doping property was evident. The ZnO:N film showed p-type conductivity with hole carrier concentration of 1×10^{16} cm^{-3} and hole mobility of 8.6 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ at room temperature. The I-V characteristics of ZnO homojunction confirm a rectifying diode behavior. This work indicated that the hydrothermal treatment was an effective and practicable method to fabricate the p-type ZnO thin film.

This work was supported by the Key Project of the National Natural Science Foundation of China under Grant No. 50532050, the "973" Program under Grant No. 2008CB317105, the Knowledge Innovation Program of the CAS under Grant No. KJCX3.SYW.W01, the Innovation Project of the Chinese Academy of Sciences, and the National Natural Science Foundation of China under Grant Nos. 60506014, 10874178, and 60776011.

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