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Boron and nitrogen co-doped ZnO thin films for opto-electronic applications

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Abstract

The transparent conductive oxides such as ZnO have been widely studied due to their potential applications. As a promising wide band gap semiconductor, ZnO thin films with various dopants are important in fabricating the photonic devices to meet the various needs. In this study, boron and nitrogen co-doped ZnO thin films were fabricated at different temperatures (100–600 °C) on sapphire (0 0 1) substrates using pulsed laser deposition technique. X-ray diffractometer, atomic force microscope, spectrophotometer and spectrometer were used to characterize the structural, morphological and optical properties of the thin films. Hall measurements were also carried out to identify the electrical properties of the thin films.

Keywords: Thin film; Properties and stokes shift; BN-doped ZnO

1. Introduction

ZnO is an important wide band gap semiconductor material, which has a direct wide band gap of 3.3 eV and large exciton binding energy of 60 meV at room temperature [1]. The band structure and optical properties of ZnO are very similar to those of GaN. The similarity in properties between ZnO and GaN makes ZnO one of the most promising materials for photonic devices in the ultraviolet range. Moreover, the binding energy of the exciton of ZnO is larger than that of GaN at room temperature. This is another advantage of ZnO that has over GaN for exciton-related device applications. Concurrently, as a transparent conductive oxide, ZnO can be used as transparent conductive films, solar cell windows, and bulk acoustic wave devices [2–5]. Therefore, ZnO related materials have received considerable attention [6–13].

For realization of optical devices based on ZnO, growing both n-type and p-type ZnO is necessary. Most semiconductors including ZnO naturally show n-type conduction. The n-type ZnO thin film is very easy to be fabricated, and the conductivity can be controlled by doping with different materials and with different doping levels. However, the p-type ZnO seems to be difficult to achieve. Among the wide band gap semiconductors, addition of impurities often induces dramatic changes in their electrical and optical properties [14–17]. Some researchers reported that the p-type ZnO was achieved by different doping methods. However, few results can be repeated by other groups, or the property of the achieved p-type ZnO is difficult to be used for the device fabrication. So, achieving p-type ZnO with satisfied properties attracts a lot of researchers' attention. In this study, we attempted to fabricate the p-type ZnO thin film using the boron and nitrogen co-doping method by using PLD technique, the doping effects of BN on the structural and optical properties of ZnO thin films were observed and discussed.

2. Experimental procedure

PLD system used in this study had been described in our previous papers [18,19]. The energy density of the excimer

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laser was set at ~0.8 J/cm^2. The ablated material was then deposited on substrate held at 53 mm above the target. High-purity BN powder (0.2 at.%) was evenly mixed with ZnO powder, and the target making method had been described in former papers. During the deposition, the conditions were as follows: the repetition frequency of the laser was 5 Hz; the background O_2 pressure was 100 mTorr; and the substrate temperature varied from 100 to 600 °C. The deposition time was 1 h. In this condition, the thickness of the thin film was about 200 nm. After deposition the thin films were cooled naturally to room temperature for various measurements.

The crystalline structures of the thin films were studied by an x-ray diffraction (XRD, X'pert MPD, Panalytical, 40 kV, 30 mA) measurement using Cu Kα1 radiation with $\lambda = 1.5406$ Å. The surface morphology of the thin films was investigated by a scanning probe microscope in the AFM mode (SPA-400, Seiko Instruments). The electrical parameters of the thin films were measured by van der pauw method at room temperature using the Hall effect measurement system. The transmittances of the thin films were measured by a UV–vis-IR spectrophotometer (Vary-5, Australia) in the wavelength range of 300–700 nm. The excitation source used in photoluminescence (PL) measurements was a He-Cd laser operating at 325 nm with an output power of 30 mW.

3. Results and discussion

Fig. 1 shows XRD patterns of BN-doped ZnO thin films deposited at different temperatures on sapphire (0 0 1) substrates. The *y*-axis was plotted in log scale. The growth temperature was important in determining the crystal structures. Except for the sapphire (0 0 6) peak, the (0 0 2) orientation was observed in all of the thin films. However, the (0 0 2) peak intensity increased with increasing growth temperature. This increase of the (0 0 2) peak intensity meant that the film quality was improved with increasing growth temperature. As seen that, the ZnO (0 0 4) peak appeared in the thin films grown at the temperatures higher than 300 °C and the intensity increased with growth temperature. As the growth temperature was increased up to 500 °C, one more peak of ZnO (1 0 1) was observed.

The surface morphology of the thin film was investigated by a scanning probe microscope (SPA-400, Seiko Instruments) in AFM mode. The scanning area was 2 μm × 2 μm. The AFM images of the thin films had no apparent change in the view of the naked eye. So, as an example, the AFM images of the thin films grown at 100 and 600 °C are shown in Fig. 2. The values of grain size, mean diameter, and root mean square (RMS) investigated by AFM are listed in Table 1. From the table, the grain size and the surface roughness slowly increased with temperature. With the increase of the growth temperature, the

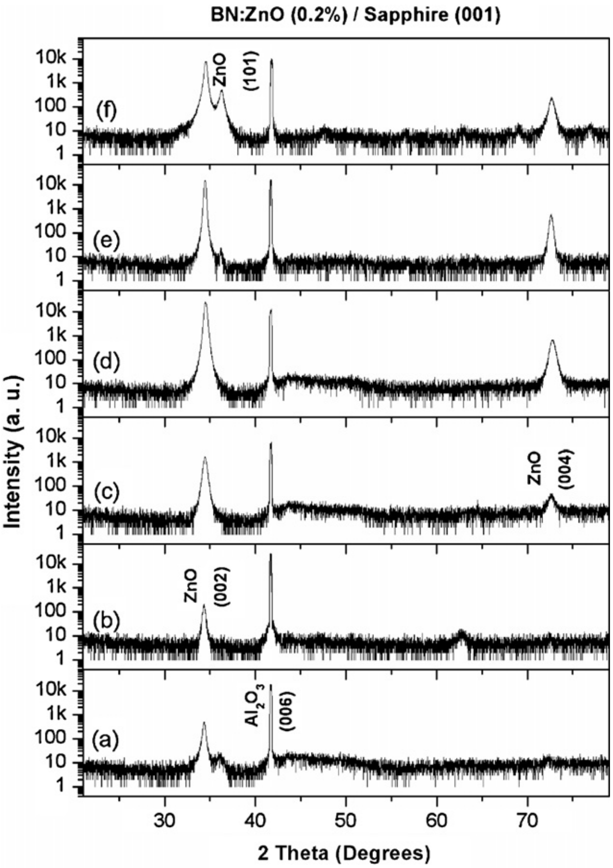

Fig. 1. XRD patterns of BN-doped ZnO (0.2 at.%) thin films grown at various temperatures on sapphire (0 0 0 1) substrates by using PLD.

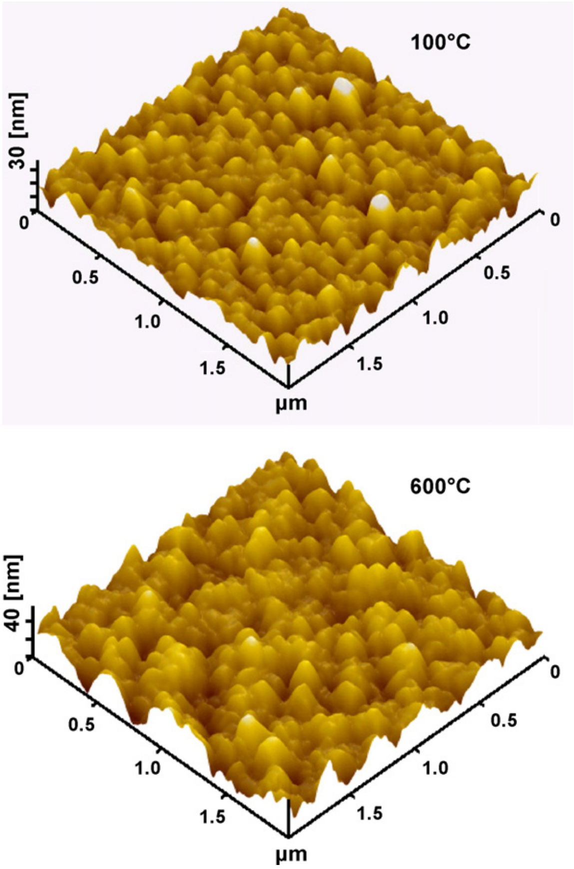

Fig. 2. AFM images of BN-doped ZnO (0.2 at.%) thin films grown at various temperatures on sapphire (0 0 0 1) substrates by using PLD.

Table 1
Grain size, grain mean diameter, and roughness of BN-doped ZnO (0.2 at.%) thin films deposited at various temperatures on sapphire (0 0 0 1) substrates by using PLD

Sample (°C)	Grain size ($\times 10^4$ nm^2)	Mean diameter (nm)	RMS (nm)
100	1.53	140	2.97
200	2.29	171	3.02
300	2.38	177	3.97
400	3.22	203	5.02
500	3.60	214	6.08
600	4.34	235	7.67

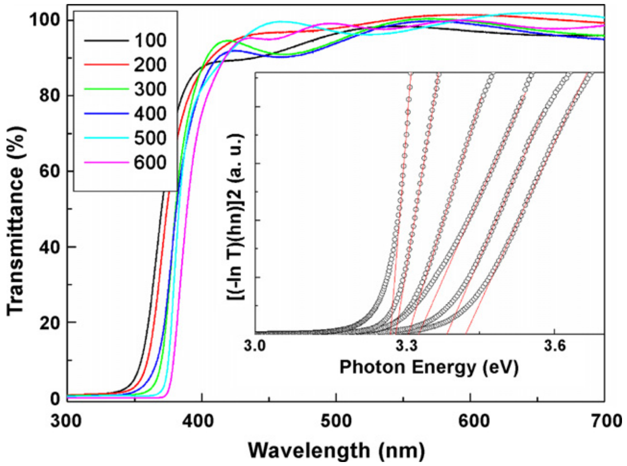

Fig. 3. Transmittances of the BN-doped ZnO (0.2 at.%) thin films grown at various temperatures on sapphire (0 0 0 1) substrates by using PLD.

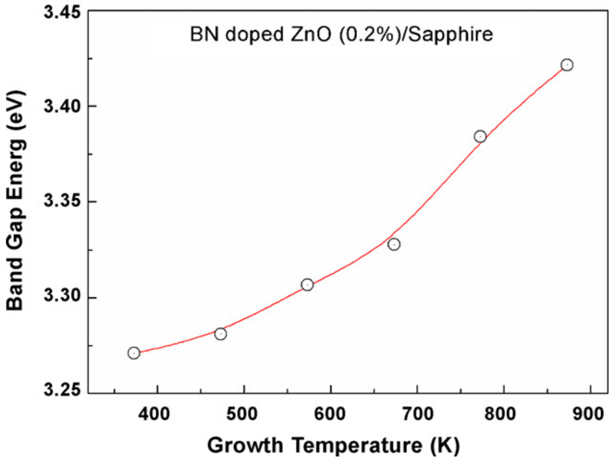

Fig. 4. Band gap energies of the BN-doped ZnO (0.2 at.%) thin films grown at various temperatures on sapphire (0 0 0 1) substrates by using PLD.

mean diameter of the grain increased from 140 to 235 nm. This can also be explained by the mobility changes of the particles at different growth temperatures. The higher the growth temperature is, the higher is the mobility. The particles with higher mobility are easy to form larger-size grains. As a result of grain size changing, as can be seen in the table, the surface roughness of the thin film increased from 2.97 to 7.67 nm for the thin film grown at 100 and 600 °C, respectively.

Hall effect measurements were carried out at room temperature to investigate the electrical properties of BN-doped ZnO thin films, and the electrical parameters are shown in Table 2. Note that the electrical parameters could not be measured for the thin films grown at 100 and 600 °C using this facility. The values of the electrical parameters were beyond the measurement ranges. All of the thin films were n-type semiconductors, and the carrier concentration decreased from 10^{20} to 10^{18} cm^{-3} as the growth temperature increased from 200 to 500 °C. The resistivity for the thin film deposited at 200–400 °C was in the range of 10^{-2} Ω cm, however, the resistivity of the thin film deposited at 500 °C was as high as 2.66 Ω cm. The thin film deposited at 400 °C had the highest mobility and the largest Hall coefficient.

A spectrophotometer (Cary-5, Australia) was used to measure the transmittances of the thin films in the wavelength range of 300–700 nm, and the transmittance spectra are shown in Fig. 3. All of the thin films deposited at various temperatures showed as high as 95% optical transmission in the visible range. This is important for applications such as transparent conductive films and solar cell windows. The sharp absorption edges were observed in all of the thin films. This meant that the thin films deposited were of high quality. The oscillation of the transmission spectra originates from the interference of the lights that refracted from the surface of the thin film and the interface. The two lights from the two faces will interfere destructively or constructively and make contribution to the oscillation of the transmittance spectra. The oscillation part of the spectra can be used to calculate the refractive index and thickness of the thin film [18].

ZnO is a direct band gap semiconductor, and boron nitride is an indirect wide band gap semiconductor. In this experiment, the doping concentration of boron nitride was as small as 0.2 at.%, and the absorption coefficient $\alpha \propto -\text{In}\, T$. So we made a plot of $[\alpha \times (hv)]^2$ against the photon energy hv. The inset of Fig. 3 shows the relative absorption coefficients of the BN-doped ZnO thin films deposited at various temperatures. The

Table 2
Electrical parameters of BN-doped ZnO (0.2 at.%) thin films deposited at various temperatures on sapphire (0 0 0 1) substrates by using PLD

Sample (°C)	Resistivity (Ω cm)	Mobility (cm^2/V s)	Carrier density (cm^{-3})	Hall coefficient (m^2/C)
100	–	–	–	–
200	9.58×10^{-2}	0.57	-1.38×10^{20}	−0.05
300	4.94×10^{-2}	2.21	-5.78×10^{19}	−0.11
400	1.77×10^{-2}	3.99	-3.87×10^{19}	−7.04
500	2.66	0.37	-6.61×10^{19}	−1.01
600	–	–	–	–

sharp absorption edge can be accurately determined for the high-quality thin film by a linear fit. As indicated in the inset of Fig. 3 that the band gap energies of BN-doped ZnO thin films could be calculated by fitting the sharp absorption edges.

The band gap energies of BN-doped ZnO thin films deposited at various temperatures were calculated and were plotted in Fig. 4. It was observed that the band gap energy of BN-doped ZnO thin film increased with increasing growth temperature. The band gap energy of the thin film deposited at 100 and 600 °C was 3.27 and 3.43 eV, respectively. The band gap energy of BN-doped ZnO thin film was larger than that of un-doped ZnO thin film [20]. This is believed to be caused by Burstein-Moss effect because of the doping of boron nitride [21]. Boron nitride is a wide band gap semiconductor with the band gap of ~6.0 eV. ZnO is naturally n-type material, and the Fermi level will be in the conduction band when it is doped. The doping concentration was 0.2 at.% and the carrier concentration was around 10^{20} cm^{-3}. The donor electrons occupy states at the bottom of the conduction band. Since the Pauli principle prevents double occupancy of states and the optical transitions are vertical, the low-energy transitions are blocked. The blockage of the low-energy transitions is known as the Burstein-Moss effect, and the absorption edge should shift to the higher energy side after doping.

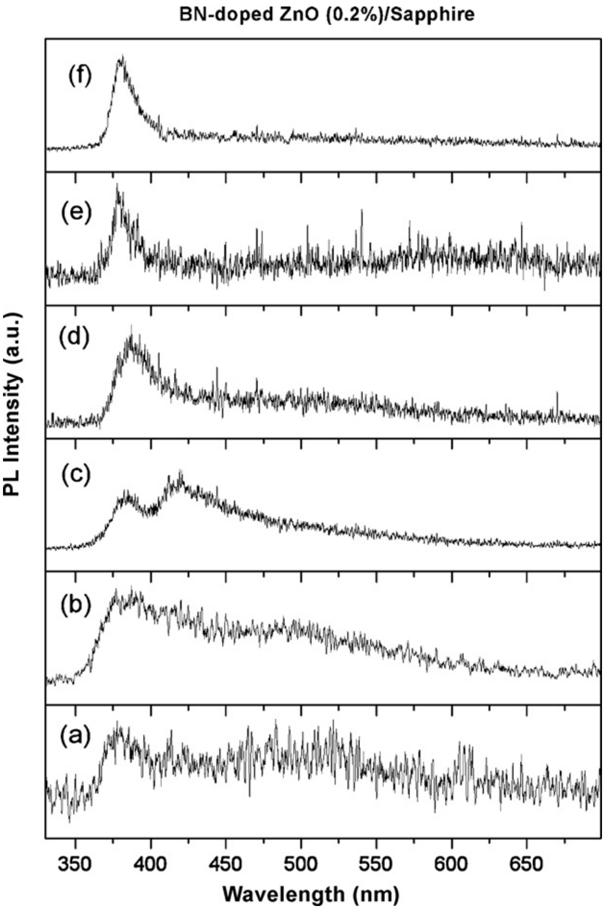

Fig. 5. PL spectra of the BN-doped ZnO (0.2 at.%) thin films grown at various temperatures on sapphire (0 0 0 1) substrates by using PLD.

PL measurements were carried out at room temperature to study the luminescent properties of BN-doped ZnO (0.2 at.%) thin films. Fig. 5 shows the PL spectra of the thin films grown at various temperatures by using PLD. It was found that all of the thin films showed near band edge (NBE) emission, and the intensity of NBE emission increased with increasing growth temperature. However, the intensity of the NBE emission of the BN-doped ZnO thin film was much weaker than that of the pure ZnO thin film deposited with the same conditions [15]. Although the doping level of BN in ZnO thin film was as small as 0.2 at.%, the NBE emission of the BN-doped ZnO thin film was greatly quenched. This is due to the generation of non-radiation recombination centers in the BN-doped ZnO thin film. The deep-level (DL) emissions were also observed in the BN-doped ZnO thin films deposited at the temperatures lower than 300 °C. However, no DL emissions appeared in the thin films deposited at temperatures higher than 400 °C. Compared with the DL emission in pure ZnO thin film deposited with the same conditions, the DL emission in BN-doped ZnO thin film was also greatly depressed. Based on our works, it was reported that the DL emission in ZnO thin film deposited by PLD originated mainly from oxygen vacancies [15]. The depressing of DL emission is due to the filling of the oxygen vacancies by nitrogen. The doping level of 0.2 at.% was enough for depressing the DL emission in such films.

Concurrently, Stokes shifts were observed in the BN-doped ZnO thin films. The value difference of the band gap energy calculated from the transmittance and the PL was called Stokes shift.

$$\Delta E = E_{\mathrm{Abs}} - E_{\mathrm{PL}}$$

According to the band gap results calculated from the transmittance spectra, the BN-doped ZnO thin films had blue shifts. However, there was no apparent band gap shifts in the PL measurements. So very large stokes shift, as large as 160 meV, was confirmed for the BN-doped ZnO thin film deposited at 600 °C.

4. Conclusions

Boron and nitrogen co-doped ZnO thin films (0.2 at.%) were deposited on sapphire (0 0 1) substrates at different temperatures (100–600 °C) using PLD technique. XRD measurements indicated that all of the thin films had a preferred (0 0 2) orientation. The peak intensity of the (0 0 2) orientation increased with temperature. New orientations of (0 0 4) and (1 0 1) were also observed in the BN-doped ZnO thin film deposited at high temperatures. The grain size and surface roughness of the thin films, investigated by AFM, increased slowly with increasing growth temperature. The Hall measurements indicated that all of the thin films were n-type semiconductors and the carrier concentration decreased from 10^{20} to 10^{18} cm^{-3} as the growth temperature increased from 100 to 500 °C. The resistivity for the thin film deposited at 200–400 °C was in the range of 10^{-2} Ω cm, however, the resistivity of the thin film deposited at 500 °C was as high as 2.66 Ω cm. The thin film deposited at 400 °C had the highest mobility and the largest Hall coefficient. The thin films showed very high transmittances and sharp absorption edges. The band gap energies of the thin films were calculated by fitting the absorption edges. The band gap energy of BN-doped ZnO thin film increased with temperature. The band gap energies were larger than the pure ZnO due to Burstein-Moss effect. PL measurements showed that both the NBE emission and DL emission were quenched by doing boron and nitrogen into ZnO thin film. The generation of non-radiation recombination centers was responsible for the quenching of the NBE emission in the BN-doped ZnO thin films, and the depressing of the DL emission was due to the filling of the oxygen vacancies by nitrogen.

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