Red-shift of the photoluminescence peak of N-doped ZnO phosphors

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Abstract

ZnO films were fabricated using rf-magnetron sputter deposition process with different N_2 ambient. N-content in N-doped ZnO films was less than 1%. The wavelength of the highest intensity PL peak of N-doped ZnO was shifted to higher wavelength with increasing N_2 flow rate in the deposition ambient. These results indicated that the optical property of ZnO was significantly affected by the defect level created by doping with a very small amount of N.

1. Introduction

ZnO has been studied as a luminescent material for a long time, and there have been a lot of reports on their luminescent properties. However, most of these reports are focused on ultraviolet (UV) emission properties because ZnO is a good candidate material for UV LEDs [1] and UV phosphors [2]. Many research groups have employed various methods for enhancing UV emission [3, 4]. The green light cathodoluminescence (CL) of ZnO:Zn is also very attractive due to its high luminescent efficiency under low-voltage (10–1000 V) excitation [5]. For improving and altering the luminescence property of ZnO, some research groups have investigated the addition effect of group-I, -III, and –V elements [6, 7]. However, few studies are reported about the influence of N_2 in deposition ambient on the optical properties in ZnO thin films.

In this work, ZnO films were deposited using rf-magnetron sputter deposition that is a proper technique for a uniform and large-area deposition, and N_2 gas was chosen as N-source because N_2 is non-toxic and low cost inert gas. The influence of N-addition on the optical properties of ZnO films was investigated using UV-Vis spectroscopy, and photoluminescence (PL).

2. Experimental

ZnO thin films were deposited on 100 nm-thick SiO_2 coated Si substrate with a thickness of 150 nm at 200^{o}C using rf-magnetron sputter deposition technique under various ratios of Ar and N_2. Undoped ZnO (99.99 %) was used as the target of ZnO film deposition. ZnO films were annealed at 400^{o}C under pure O_2 ambient in the deposition chamber. Auger electron spectroscopy (AES) was utilized for the composition analysis of the ZnO films. The UV-Vis absorbance and transmittance of ZnO films were obtained using UV-Vis spectroscopy. In the room temperature PL measurement, HeCd laser was used as a light source. The excitation wavelength and the power were 325 nm and 20 mW at room temperature, respectively.

3. Results and discussion

The structural parameters such as grain size and lattice parameter were extracted using ZnO (002) XRD peaks in our previous work. The result revealed that the crystallinity was degraded and the tensile stress was increased due to N-addition in the films

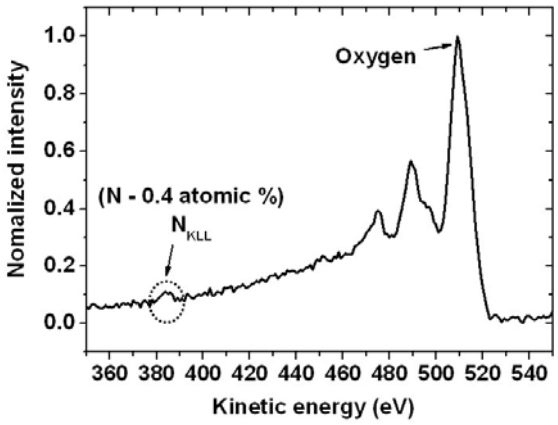

Figure 1. N_{KLL} AES spectrum of ZnO film deposited under 5 sccm N_2 ambient.

(the data not shown here) [8].

Figure 1 shows N_{KLL} AES spectrum of ZnO film deposited under 5 sccm N_2 ambient. The composition analysis using AES showed that N content was 0.4 % in the ZnO film. The result confirmed the existence of N in ZnO thin film deposited under N_2-added ambient.

UV-Vis transmittance spectra of undoped and N-doped ZnO films deposited on the quartz substrate were obtained for wavelengths of 350–700 nm as shown in Fig. 2. The average transmittance in the visible spectrum (400–700 nm) was 83% after deposition of the undoped ZnO film as shown in Fig. 2. All the films had a fundamental absorption edge around 380 nm (3.26 eV).

The absorbance of ZnO films was obtained from UV-Vis transmittance. The absorbance data of the ZnO films were utilized to determine the band-gap of the films. To determine the optical band-gap, the model for direct inter-band transitions: $\alpha h\nu = C(h\nu - E_g)^{1/2}$, was used to obtain the optical band-gap of N-doped ZnO films [9]. Where C is a constant, $h\nu$ is

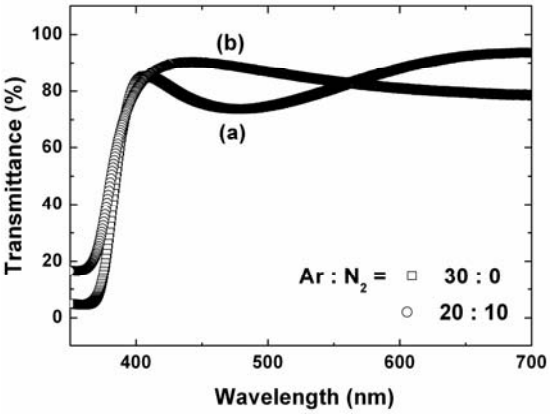

Figure 2. Optical transmittance as a function of wavelength for (a) undoped and (b) N-doped ZnO film

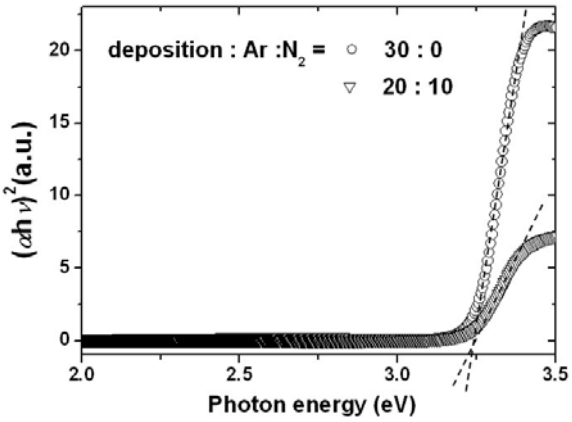

Figure 3. A plot of $(Ah\nu)^2$ vs $h\nu$ for determining the direct band gap of ZnO films.

photon energy, E_g is the optical band-gap, and α is the absorption coefficient. Although, the absorption coefficient have to be calculated by formula: T (%) = exp(−αd), where T is transmittance and d is the thickness of the film, we use the absorbance, A, in Fig. 3 instead of absorption coefficient because these two samples had the same thickness. In this approximation, $(Ah\nu)^2$ is a linear function of $h\nu$. The E_g value can be obtained by extrapolating the linear portion to $(Ah\nu)^2 = 0$ as shown in the Fig. 3. The calculated optical band-gap of undoped and N-doped ZnO thin film was nearly equal to 3.25 eV. These band-gap values are smaller than the well-known band-gap of 3.30 eV for single crystal ZnO [10].

The effect of N-doping on the luminescent property of ZnO films was investigated by PL measurement with excitation wavelength of 325 nm. Figure 4 (a) shows room-temperature PL spectra of the samples deposited with different N_2 content. All three samples exhibited near-band-edge (NBE) UV emissions at approximately 380 nm (3.26 eV). The result is well consistent with the optical band-gap (3.25 eV) obtained using UV-Vis spectroscopy. Undoped ZnO film showed no emission in visible region which was consistent with earlier works on undoped ZnO films [11]. Contrarily, N-doped ZnO samples exhibited the broad emissions in visible region. These broad emissions in visible region can be ascribed to the transitions of the excited optical centers from the deep level to the valence band, and the deep level is possibly related to the defects in N-doped ZnO films [12]. The defect-related broad peak centered near 600 nm (2.06 eV) in the ZnO film deposited under 5 sccm N_2 ambient. The earlier work had reported that the 2.21 eV (561 nm) band behaves as a part of the valence band, resulting in band-gap narrowing of ZnO and this deep level is one origin of visible-light

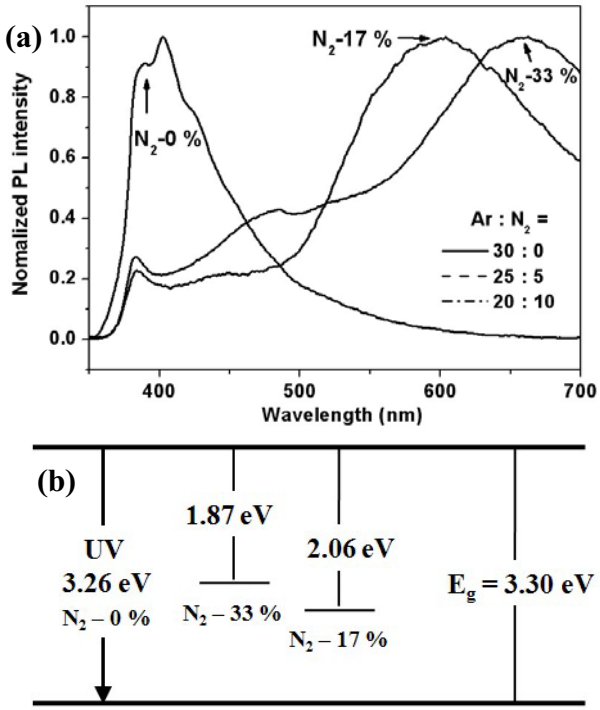

Figure 4. (a) Room-temperature PL spectra of ZnO thin films deposited under various N_2 content, (b) The Schematic of N-related defect level in ZnO film.

sensitivity in N-doped ZnO [13].

The position of the highest PL intensity peak of N-doped ZnO was shifted from 600 (2.06 eV) to 660 nm (1.87 eV) with increasing N_2 flow rate from 5 (17 %) to 10 sccm (33 %) in the deposition ambient.

Figure 4 (b) illustrates the schematic of N-related defect level in ZnO band-gap which was based on the PL result of Fig. 4 (a). The UV emission at 3.26 eV corresponds to the band-gap of the ZnO film deposited under pure Ar ambient. The defect levels near 2.06 eV and 1.87 eV are originated from the N-addition in ZnO film. The shallower donor level is formed with larger N_2 content in the deposition process.

From this result, we can deduce that the energy state of N-related defect level in ZnO can be changed with varying N_2 content in deposition ambient, resulting in the change of optical properties in ZnO, and the N_2 content in deposition process plays a significant role in determining the wavelength of visible-light emitted from ZnO.

4. Summary

In summary, ZnO thin films were deposited using RF magnetron sputter deposition process with various ratios of Ar and N_2 and annealed at 400°C. The UV-Vis transmittance and absorbance spectra showed the optical band-gap of ZnO film was 3.25 eV. While undoped ZnO showed no emission in visible region, N-doped ZnO exhibited the broad emissions in PL measurement. Red-shift of defect-related peaks was also observed with increasing N_2 flow rate from 5 to 10 sccm in the deposition ambient. These results indicated that the N-related defect level affects the optical properties of N-doped ZnO films although the N-content in the film was less than 1 %, and the energy state of the defect level can be controlled by varying N_2 content in the deposition ambient.

5. References

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