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Influence of annealing on the structural and optical properties of ZnO films grown by MOCVD

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ABSTRACT

The properties of ZnO films grown on Si (1 1 1) substrates by Metal-Organic Chemical Vapor Deposition technique using diethylzinc and H_2O as reactant gases are reported. The primary focus is on understanding the origin of deep-level luminescence. As increasing the annealing temperature, a visible emission is observed both in samples annealing in oxygen atmosphere and nitrogen atmosphere. In addition, this broad defect emission becomes obviously asymmetric when the annealing temperature was increased to 1000 °C in oxygen atmosphere. Theoretical investigations have reported that the formation enthalpy of defects is varied under different conditions. With these results, it is suggested that the visible emission in ZnO films annealed in oxygen atmosphere is related to zinc vacancy and oxygen interstitial defects. While, the green emission in ZnO films which were annealed in nitrogen atmosphere is attributed to oxygen vacancy defects.

1. Introduction

As a wide band-gap semiconductor material, ZnO is of great interest for photonic applications such as short-wavelength lasers and light-emitting diodes [1,2]. And thus, the optical properties of different forms of ZnO (single crystals, thin films, powders, and nanostructures) have been extensively studied [3–6]. It is commonly known that there are two emission peaks centering at the UV and the visible region in the room-temperature photoluminescence (PL) spectra of ZnO. The UV emission is attributed to an exciton transition. However, the mechanism of the visible emission has not been clearly delineated. Normally, the visible bands are attributed to deep-level defects in ZnO, such as vacancies and interstitials of zinc and oxygen. For example, according to Vanheusden et al. work, the green emission at 510 nm was due to the recombination of the photo-generated hole with the singly ionized oxygen vacancy [7]. While, Zhao et al. investigated the deep-level emissions in bulk ZnO samples, and concluded that the zinc vacancy is responsible for the observed white light emission band [8]. Studenikin and Cocivera assigned the green photoluminescence in ZnO to an electron-hole recombination involving a donor–acceptor complex, which most likely consists of an oxygen vacancy and a zinc vacancy [9]. Xu et al. attributed the green emission to a radiative recombination of donor levels Zn_i to acceptor levels V_{Zn} [10]. Our co-workers' calculation suggested that the green emission at 520 nm in ZnO is derived from an electron transition from the bottom of the conduction band to the antisite defect O_{Zn} level [11]. Recently, Heo et al. proposed that the green emission is related to the donor-deep acceptor (Zn vacancy $V_{Zn}{}^-$) and the yellow to the donor-deep acceptor (oxygen vacancy $O_i{}^-$) [12]. Moreover, many theoretical investigations have also been reported in order to provide the energy levels of intrinsic and extrinsic defects in ZnO [13,14]. From the above, the identification of the recombination centers and mechanisms responsible for the broad defect emission are still a matter of controversy. According to the theoretical calculation using the density-functional theory, the formation enthalpy of native defects is varied under different conditions [15]. Therefore, it is possible that the visible luminescence in ZnO has different origins in different samples. In addition, most of the previous literatures utilized CO_2 or O_2 or O_2 plasma as an oxygen source [11,12,16]. Recently, several reports demonstrated a number of possibilities for yielding high-quality ZnO films via a small amount of H_2O vapor assistance, suggesting that H_2O vapor might be an efficient new oxygen source for the growth of ZnO [17–19]. And considering that only a small investment will be necessary as H_2O vapor is an abundant natural resource. In this work, diethylzinc (DEZ) and H_2O were used as

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reactant gases. ZnO films were deposited by Metal-Organic Chemical Vapor Deposition (MOCVD) technique on Si (1 1 1) substrates. The as-deposited films were annealed at different atmospheres and temperatures. The variation of structural and optical properties induced by post-annealing are investigated and the results are discussed related with the origin of the so-called green emission.

2. Experimental procedure

ZnO films were deposited on Si (1 1 1) substrates by the MOCVD technique. Diethylzinc and H_2O were used as source materials. They were supplied to the growth chamber through bubbling systems using high purity nitrogen as carrier gas. During growth, DEZ and H_2O were kept in bubblers at −10 °C and 2 °C, respectively. In order to eliminate the remnant amorphous silica layer thoroughly, the Si substrates were bombarded by Ar+ plasma in the growth chamber before the deposition of ZnO films [20]. At first, low temperature buffer layers were deposited at 200 °C for 5 min, and amorphous ZnO layers were obtained. Then the temperature of the substrates was raised to 400 °C and the growth process maintained for 25 min. The flow rate of DEZ and H_2O were both fixed at 5 sccm (standard-state cubic centimeter per minute). The thickness of the obtained ZnO film was about 300 nm. In order to investigate the effect of annealing treatment, the as-grown ZnO films were annealed in an oxygen atmosphere (1 atm) or in a nitrogen atmosphere (1 atm) for 1 h under the temperatures range from 800 °C to 1000 °C. The crystallinity of obtained samples was analyzed by X-ray diffraction (XRD) using a D-MAX/γA system with Cu*K*α radiation λ = 0.154178 nm in the range of 30–80°. And the optical properties of ZnO films were characterized by photoluminescence with He–Cd laser as a light source using an excitation wavelength of 325 nm.

3. Results and discussion

The XRD patterns of ZnO films annealed in different atmospheres at 800 °C, 900 °C and 1000 °C are shown in Fig. 1(a) and (b). All the peaks of the XRD patterns can be indexed to ZnO with the hexagonal wurtzite structure. No excess diffraction peaks of impurities are observed. Strongest intensity of the diffraction peak corresponding to (0 0 2) plane indicates that all the samples have a *c*-axis preferential orientation. In addition, for the ZnO films annealed in O_2, the intensity of (0 0 2) diffraction peak enhanced with increasing temperature and reaches to the extreme at 900 °C, after that it decreased at 1000 °C. While, for the samples annealed in N_2, the intensity of diffraction peak increased consistently as the annealing temperature was increased from 800 °C to 1000 °C. Fig. 2 displays the variation of the full width at half maximum (FWHM) of the (0 0 2) peak along with the annealing temperatures in different atmospheres. The inset of Fig. 2 is the XRD pattern for the as-deposited film, which indicates poor crystal quality before annealing treatment. Both the maximum XRD peak intensity and the minimum FWHM of 0.19° are obtained by annealing at 1000 °C in nitrogen atmosphere. These results indicate that the annealing temperature and atmosphere have a great influence on the structure of the samples and relatively better structural quality of ZnO films were obtained when annealed in nitrogen atmosphere. Chongmu Lee also reported that nitrogen annealing offers better crystallinity than oxygen annealing at the same annealing temperature [21].

Fig. 3 illustrates the PL spectra of ZnO films annealed in oxygen at 800–1000 °C. As shown in the figure, the spectrum can be divided into the UV and the visible light parts. For the sample annealed at 800 °C, only a UV emission peak can be observed. As increasing the annealing temperature, a broad visible peak center around 550 nm appeared and it becomes obviously asymmetric when the annealing temperature was increased to 1000 °C. It should be noted that this broad visible peak can be deconvoluted into two Gaussian peaks, as shown in Fig. 4. One peak is still center around 550 nm, and the other peak is center around 620 nm. This orange-red emission has been found in oxygen-rich ZnO films, and it is attributed to oxygen interstitial defects [22]. For the green emission, there are various suggestions, such as oxygen vacancy, zinc vacancy, interstitial zinc, interstitial oxygen and antisite(O_{Zn}), etc.[9–12,22].

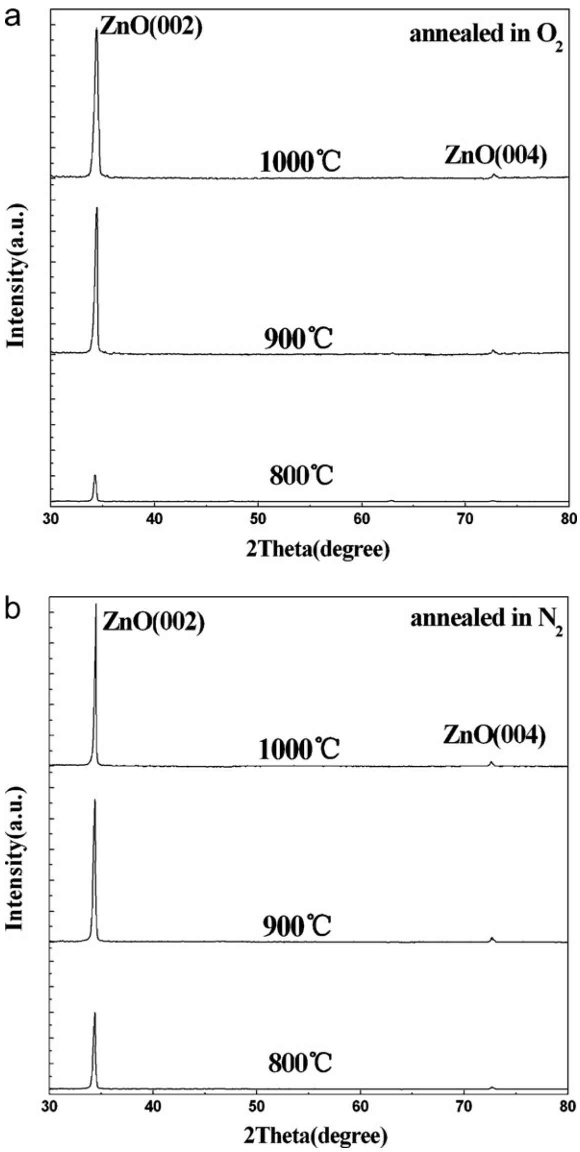

Fig. 1. (a) XRD patterns of ZnO films annealed in oxygen atmosphere at 800 °C, 900 °C and 1000 °C; (b)XRD patterns of ZnO films annealed in nitrogen atmosphere at 800 °C, 900 °C and 1000 °C.

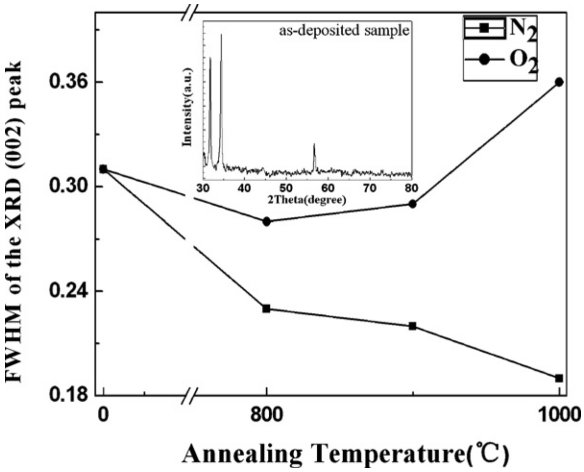

Fig. 2. The FWHM of the (0 0 2) peak along with the annealing temperatures in different atmospheres. The inset is the XRD pattern for the as-deposited film.

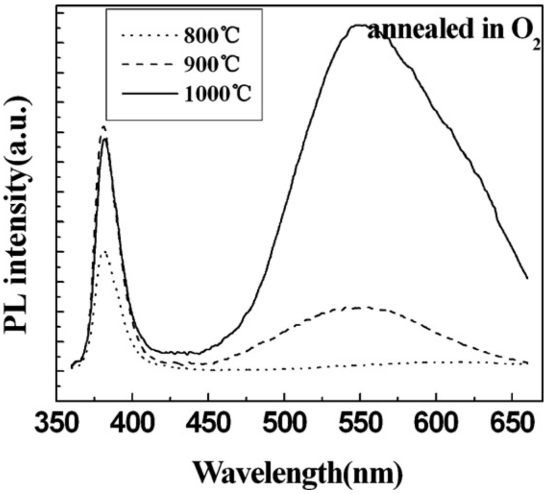

Fig. 3. PL spectra of ZnO films annealed at 800 °C, 900 °C and 1000 °C for 1 h in oxygen atmosphere.

While for our samples, we suggest that this green emission band derived from zinc vacancy. It is because that when ZnO films were annealed in oxygen-rich conditions, oxygen vacancies were compensated effectively. Furthermore, more Zn atoms were evaporated during annealing and leading to the formation of zinc vacancies. As increasing the annealing temperature further, new defects of oxygen interstitials were created [23]. In addition, during the annealing treatment of ZnO films in oxygen atmosphere, the possible changes of defects with the oxygen pressure could be described as follows:

$$V_O + \frac{1}{2}O_2(g) = O_o \Rightarrow [V_O] \propto P_{O_2}^{-1/2} \tag{1}$$

$$Zn_i + \frac{1}{2}O_2(g) = Zn_{Zn} + O_o \Rightarrow [Zn_i] \propto P_{O_2}^{-1/2} \tag{2}$$

$$\frac{1}{2}O_2(g) = V_{Zn} + O_o \Rightarrow [V_{Zn}] \propto P_{O_2}^{-1/2} \tag{3}$$

$$\frac{1}{2}O_2(g) = O_i \Rightarrow [O_i] \propto P_{O_2}^{-1/2} \tag{4}$$

It is known that the oxygen pressure in oxygen atmosphere is much larger than that under growth conditions. Eqs. (3) and (4) indicate that concentrations of zinc vacancies and oxygen interstitials increased with the increase of the oxygen pressure P_{O_2}. Therefore, it is reasonable to attribute the broad peak centers around 550 nm to Zn vacancies and the other peak centers around 620 nm to oxygen interstitials. The intensity of UV emission peak increased at 900 °C and then decreased at 1000 °C indicates the variation of crystal quality. It is consistent with the results of XRD.

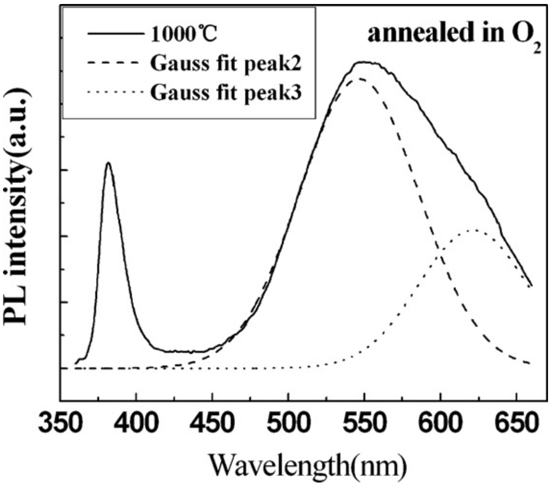

Fig. 4. PL spectra of Gaussian fits of the defect emission after annealing at 1000 °C in oxygen atmosphere.

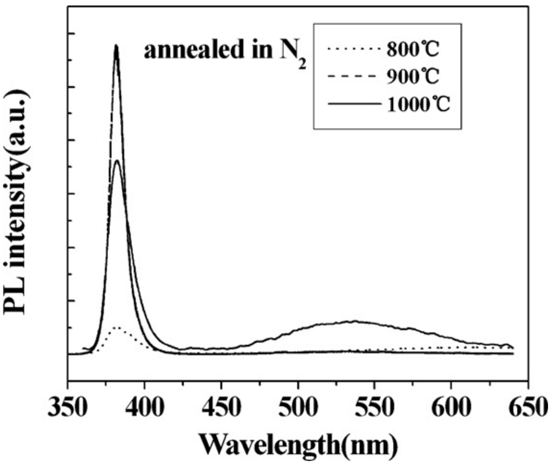

Fig. 5. PL spectra of ZnO films annealed at 800 °C, 900 °C and 1000 °C for 1 h in nitrogen atmosphere.

Fig. 5 shows the PL spectra for the ZnO films annealed in nitrogen atmosphere at different temperatures. Only a broad peak is obtained in the UV region when the sample was annealed at 800 °C. Then this peak is enhanced significantly and its line width is considerably narrower at 900 °C indicating better crystal quality. Since the PL line width of binary compound is dominated by the inhomogeneity of the sample, except the phonon interaction, the narrow PL line width is regarded as a clear evidence of crystal quality improvement. While, as increased the annealing temperature to 1000 °C, the intensity of the UV emission peak decreased and a weak defect-band emission in the visible region is observed. Studenikin has reported that when ZnO films were annealed in nitrogen atmosphere, low concentration of oxygen leads to the formation of oxygen vacancies and zinc interstitials more easily [24]. The creation of oxygen vacancies and zinc interstitials is thermodynamically more favorable than that of zinc vacancies and oxygen interstitials. Therefore, the deep-level emission might be independent of zinc vacancies and oxygen interstitials. In addition, many reports have proposed that the radiative recombination related to zinc interstitials locates at violet region [11,25–27]. Thus, we suggest that the appearance of this green emission is strongly related to the increase of the oxygen vacancy concentration by high temperature annealing process.

4. Conclusions

ZnO films have been grown on Si (1 1 1) substrates by Metal-Organic Chemical Vapor Deposition technique using diethylzinc and H_2O as reactant gases. XRD and PL results indicate that relatively better structural quality and optical properties of ZnO films were obtained when annealed in N_2 atmosphere. Through the analysis of PL results, it is proposed that the visible emission in oxygen-rich ZnO films is related to zinc vacancy and oxygen interstitial defects. While, the green emission in ZnO films which were annealed in nitrogen atmosphere is attributed to oxygen vacancy defects. Further research is needed. More work should be performed to figure out the dominant luminescent center for the visible emission of different ZnO films.

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