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Bright green emission and temperature dependent localized bound exciton transitions from undoped ZnO films

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ABSTRACT

Bright green luminescence is achieved from undoped ZnO films prepared by the reaction of oxygen and zinc powder. The green emission band is considered to be mainly due to the singly ionized oxygen vacancies. Temperature dependence of exciton transitions in the undoped ZnO films has been investigated in the range from 10 to 270 K. The PL spectrum at 10 K is dominated by neutral donor-bound exciton (D°X) emissions. The dominant emission centered at about 3.303 eV at above 45 K can be attributed to the localized bound exciton (LBX) transitions related to basal plane stacking faults. LBX transitions can survive up to near room temperature due to the LBX binding energy of 68 meV.

1. Introduction

Optical property study in the wide-bandgap ZnO semiconductor materials has been of increasing interest because of its significance for the device applications such as short wavelength ultraviolet (UV) laser diodes (LD), light emission diodes (LED), transparent electrodes and so on [1,2]. Photoluminescence (PL) spectroscope is a nondestructive and sensitive tool to investigate the characteristics of ZnO materials with diversified morphology. Especially low-temperature PL can be employed to explore the evolution process of exciton transitions associated with impurities, dopants and defects. The large free exciton (FX) binding energy (approximately 60 meV) in ZnO makes it possible to realize the efficient emission from free exciton recombination even above room temperature [3]. Therefore, the near band edge (NBE) free exciton emission is generally considered as an origin of UV emission in the room temperature PL spectra [4]. The well-known defect-based green emission band in ZnO PL spectra is ascribed to singly ionized oxygen vacancies by some and to other defects or impurities by others [5–7]. In other words, the exact origin of green emissions is still in dispute, although defects such as oxygen vacancies (V_O), oxygen interstitials (O_i), zinc vacancies (V_{Zn}), zinc interstitials (Zn_i) and oxide antisites (O_{Zn}) are suggested as origin of candidates [8]. The transitions of the donor- and acceptor-bound excitons and the donor-acceptor-pair (DAP) are still ambiguous in the low-temperature PL spectra of UV range [9].

The deposition of ZnO films by chemical vapor deposition (CVD) has been attractive for a long time because of high growth rate, good surface flatness and preferred orientation [10,11]. In this work, a facile CVD technique was utilized to prepare highly orientated ZnO films by the reaction of oxygen and zinc powder without using any dopants. As-grown undoped ZnO films still has a strong green light emission even in bright background, which will promote the applications of ZnO visible light LED. It is confirmed that a large number of oxygen vacancies in ZnO films is responsible for the bright green emission peak. Temperature dependence of exciton transitions in the undoped ZnO films is also investigated in the range from 10 to 270 K.

2. Experimental

ZnO thin films were grown on (100) oriented p-Si substrates by an atmospheric pressure CVD technique using zinc powder and oxygen as source materials. The schematic diagram of CVD apparatus can be seen in our previous report [11]. The temperature of porcelain boat filled with zinc powder and p-Si substrate was maintained at 600 °C and 570 °C, respectively, so as to form a temperature gradient between the source and the substrate. Under the role of temperature gradient, ZnO films were deposited onto the (100) Si substrate by the reaction of zinc powder and oxygen with a rate of 0.2 L/min following the process:

$$Zn + O_2 \rightarrow ZnO.$$

The structural characterization of samples was carried out by X-ray diffraction (XRD) performed on a Philips X'Pert Pro Super X-ray diffractometer with $Cu_{K\alpha}$ radiation. The morphology of thin

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films was measured using a JSM-6700F field-emission scanning electron microscope (FE-SEM). X-ray photoelectron spectra (XPS) were recorded on a Thermo-VG Escalab 250 X-ray photoelectron spectrometer. Temperature dependent PL spectra were performed using a He-Cd laser with an excitation wavelength of 325 nm.

3. Results and discussion

Fig. 1(a) shows a representative XRD pattern of ZnO films grown on Si (100) substrate, which is typical of all ZnO films. A dominant (002) diffraction peak at 2θ 34.35° indicates that the as-deposited thin film is grown with c-axis preferred orientation. The full width of half maximum (FWHM) of (002) peak is about 0.2°, which implies the good crystallite quality of the film. Besides (002) peak, the (101) peak is observed, which indicates the film is polycrystalline. The existence of (101) peak was considered to be related to a great deal of oxygen vacancies contained in ZnO films [12]. From the typical FE-SEM images shown in Fig. 1(b) and (c), it can be noted that the ZnO films with strong (002) preferred orientation have average grain size of 0.6 μm with the film thickness of 0.9 μm.

In order to estimate the stoichiometric ratio deviation of ZnO films, the XPS measurements were performed and the typical XPS of Zn2p(3/2) and O1s for ZnO films are plotted in Fig. 2(a) and (b), respectively. The XPS of O1s was fitted with Gaussian distribution. The peak at 531.1 eV is ascribed to O1s in Zn-O while the binding energy at 532.6 eV corresponds to O1s of the –OH or H_2O [13]. It implies that some water infiltrated the surface of ZnO films when they were taken out from the reaction chamber. The quantitative atomic density ratio of n (O)/n (Zn) can be obtained by calculating the area of O1s (Zn-O) and Zn2p(3/2) peaks in combination with the sensitivity factor of O and Zn atoms. The ratios of n (O)/n (Zn) in the ZnO films is estimated to be 0.78, which indicates that such a serious stoichiometric ratio deviation will inevitably lead to the presence of a large number of oxygen vacancies in the undoped ZnO films.

The room temperature PL spectrum of ZnO films is shown in Fig. 3. The deep-level emission (DLE) is dominated by the strong and wide green band centered at around 2.444 eV and relatively weak UV emission located at 3.258 eV is also observed. High green luminance of the films at room temperature can be attributed to large numbers of singly ionized oxygen vacancies in ZnO. Oxygen vacancies can occur in three different charge states: the neutral oxygen vacancy (V_o^0), the singly ionized oxygen vacancy (V_o^+), and the doubly ionized oxygen vacancy (V_o^{2+}), and only V_o^+ can be used as a light emitting recombination centers [14,15]. Taking into

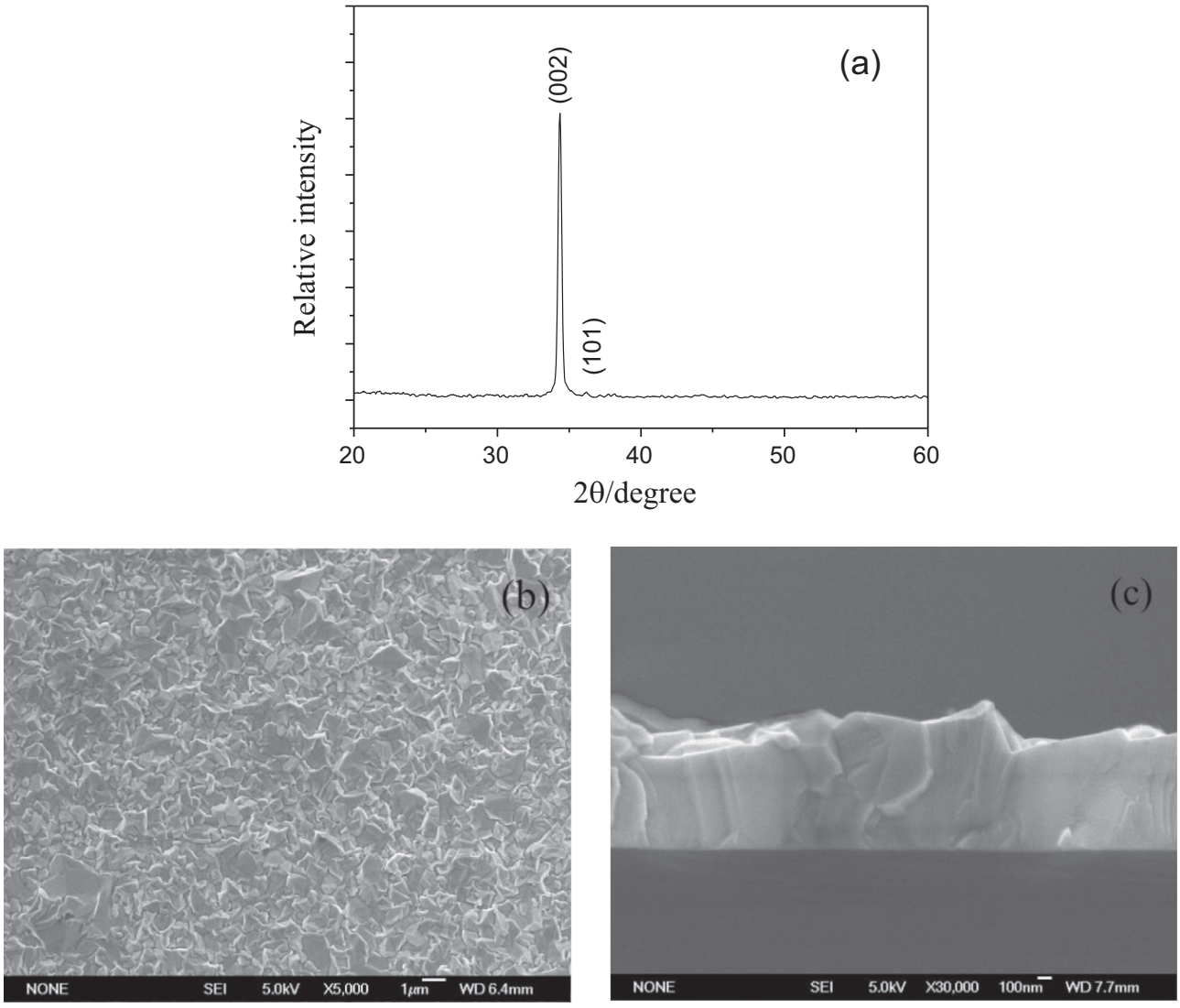

Fig. 1. (a) XRD pattern and FE-SEM images of as-deposited ZnO films: (b) surface morphology; (c) cross section.