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Effects of annealing on the crystal structures and blue emission properties of sputtered ZnO films

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ABSTRACT

ZnO films usually exhibit a complex blue emission property, but the luminescence mechanism behind the blue emission is still not clearly understood. In this study, ZnO films have been deposited on SiO_2/silicon by RF magnetron sputtering. Two blue emission peaks centered at 420 and 440 nm are found for the ZnO films. The variation of the emission intensity and the peak location was investigated at different annealing temperatures. According to the calculation of the defect levels in the ZnO films, we suggest that the 440 nm (2.82 eV) emission peak corresponds to the electron transition from the interstitial Zn to the top of the valence band; the 420 nm (2.95 eV) emission peak is due to the shallow acceptor levels of vacant Zn or interstitial O. The melting point of the ZnO grains is around 700 °C which is much lower than that of bulk ZnO (1975 °C).

1. Introduction

ZnO is a wide-bandgap II–VI semiconductor with a large exciton binding energy of about 60 meV [1]. The remarkable properties of ZnO have aroused intensive research for the potential applications of ZnO in optoelectronic devices, such as, blue/UV light emitting devices and diode lasers [2–4]. In order to improve the devices' performance, the emitting properties of the ZnO film must be studied. Different emission peaks have been found for ZnO, including UV, blue, green, yellow, red and infrared emissions [3]. The UV emissions have been attributed to near band-edge emission [5–10]. The origin of green emission bands is assigned to several intrinsic defects such as oxygen vacancy (V_O), oxygen interstitial (O_i), antisite oxide (O_{Zn}) and zinc vacancy (V_{Zn}) [6,9,11,12]. Usually, the presence of broad visible emission dominated by the green emission band indicates the presence of several point defects like V_O, V_{Zn} and O_i in the samples [9]. Recently McCluskey and Jokela have given a good review on the defect states in ZnO [13].

For the blue emission, different wavelengths of the emission peaks have been reported by several authors, for example, 412 nm by Cui et al. [14]; 420 nm by Jin et al. [6]; 430 nm by Fang et al. [15]; 440 nm by Ren et al. [16] and Fu et al. [5]. Moreover, the blue peak often changes its location with different deposit processing or post-processing of the sample, such as postannealing. Cui et al. found that the blue peaks shift from 412 to 407 nm with the increase of the postannealing temperature. The author believed that the change of stress in the films was the cause of this shift [14]. Jin et al. found that the blue emission strongly depends on the oxygen pressure, and that only the samples deposited under high oxygen pressure show the blue emission [6]. Many luminescence mechanisms have been proposed to explain the blue emission, but the luminescence mechanism behind the blue emissions is still a subject of controversy.

In this study, we focus on the effect of postannealing processing on the blue emission properties. This is because postannealing treatment, when carried out in suitable conditions, is a conventional and effective technique to reduce intrinsic defects and to improve the crystallinity [17–19]. The blue or green emission intensities reduce with the related intrinsic defects. Thus, annealing gives a way to investigate the luminescence mechanisms behind the blue or green emission [7,14,20].

2. Experimental procedure

The ZnO films were deposited on SiO_2/silicon substrates by RF magnetron sputtering using a ZnO target (99.99%) in mixture gas of Ar (99.99%) and O_2 (99.99%) with Ar/O_2 ratio 1:1. The diameter of the ZnO target is 5.0 in. The SiO_2 layers of about 500 nm thick were prepared on cleaned silicon by the thermal-oxidative technique. During film deposition, the RF power was 100 W and

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the total pressure was maintained at 1 Pa. Substrate temperature was kept at 250 °C. The sputtering time was 30 min.

The sample was then cut into five small pieces. Four of them were annealed in a quartz tube furnace at four different temperatures: 500, 700, 900 and 1100 °C. These samples were labelled as T1, T2, T3 and T4, respectively. Accordingly, the as-grown sample was labelled as T0. When the furnace was heated to each selected temperature, the sample was put into the quartz tube and kept for 60 min, then the furnace was cooled to room temperature. The cooling rate of the furnace was 1.8 °C/min from annealing temperature to 200 °C. During the annealing treatment, O_2 (99.99%) gas was flowing into the quartz tube with flow rate of 1000 SCCM.

Surface morphology observation and film thickness measurements were performed with a LEO-1530FE scanning electron microscope (SEM). The crystal structure properties of the films were investigated by using a Panalytical X'pert X-ray diffractometer (XRD) in $\theta-2\theta$ configuration with a monochromatic Cu Kα ($\lambda = 0.15406$ nm) radiation. The photoluminescence spectra of the samples were investigated at room temperature using a Hitachi F-4500 photoluminescence spectrophotometer, and the samples were illuminated at an excitation wavelength of 320 nm using a xenon lamp.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-grown and annealed ZnO films. The as-grown film is highly *c*-axis orientation. Its XRD pattern only shows a ZnO (0 0 2) diffraction peak at around 34.4°, which characterizes the hexagonal wurtzite structure of ZnO crystal. The other samples also show strong ZnO (0 0 2) diffraction peaks. The results indicate that all samples have wurtzite structure and *c*-axis preferred orientation, corresponding to vertical growth with respect to the substrate basal plane. The columnar cross-section of sample T0 also confirms the vertical growth pattern (Fig. 2). Sample T1 shows another weak peak at around 63.0°, which is indexed as ZnO (1 0 3). The other peaks of sample T2 can be indexed to (1 0 1), (1 0 2) and (1 0 3) of hexagonal structure ZnO crystal. This implies that sample T2 undergoes a recrystallization process during annealing. However, when the samples were annealed at higher temperature (900 and 1100 °C), only ZnO (0 0 2) and (0 0 4) peaks have been found. Furthermore, it is obvious that ZnO films have reacted with SiO_2 to form Zn_2SiO_4 after annealing at 1100 °C. Usually ZnO reacts with SiO_2 to form Zn_2SiO_4 at temperature above 800 °C [20].

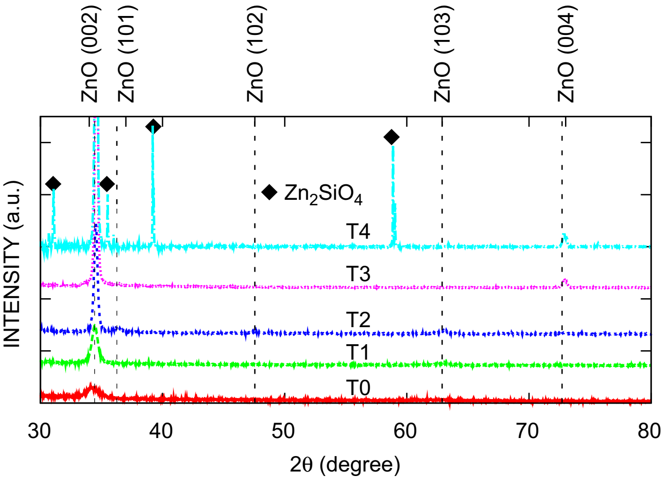

Fig. 1. XRD line profile of the samples.

The intensity of the (0 0 2) diffraction peak is improved by annealing, which indicates that the ZnO crystal grains may have grown up during the annealing. The ZnO (0 0 4) peaks shown on Sample T3 and T4 also mean they have bigger ZnO crystal grains. Because the distance of ZnO (0 0 4) planes is twice as long as the (0 0 2) planes, only bigger grains own enough (0 0 4) planes to diffract the X-ray and form a detectable X-ray line profiles. The grain size can be estimated by the Scherrer formula using FWHM value of the XRD diffraction peaks as follows [14]:

$$D = 0.9\lambda / B\cos\theta \tag{1}$$

where D, λ, θ and B are the grain size, the X-ray wavelength, Bragg diffraction angle and the FWHM of the diffraction peak, respectively. The calculated grain sizes of the samples are shown in Fig. 3. It is found that the grain size has a sharp increase, when the samples were annealed at temperature above 700 °C.

As shown in Fig. 2, annealing drastically changes the surface morphology of the ZnO films, especially at temperature above 700 °C. Fig. 2(a) shows that the ZnO grain size of the as-grown film T0 is on the order of 20–60 nm. It shows a clear interface between every two ZnO grains. The interface disappears when the annealing temperature increases (sample T3 and T4). The ZnO grains melt together when annealed at temperature above 700 °C, although the melting point of ZnO (1975 °C) is much higher than the annealing temperature [7].

Generally, materials of reduced size exhibit a property of melting points lower than that of their bulk form [8]. According to the study carried out by Su et al., ZnO nanorods (~ 20 nm in diameter, ~ 400 nm long) could start to melt at temperatures ≥ 750 °C [8]. According to the theoretical investigation by Guisbiers et al., the melting temperature T_m of the ZnO nanostructures is given by [21]

$$\frac{T_m}{T_0} = 1 - \frac{\alpha_{shape}}{2L} \tag{2}$$

where T_0 is the bulk melting temperature (K), whereas the shape parameter α_{shape} is defined as $\alpha_{shape} = 2AL(\gamma_s - \gamma_l)/(V\Delta H)$, where L is the smallest dimension of the nanostructure, A and V are the surface area and volume, respectively, for a given shape. γ_s and γ_l are the surface tensions in the solid and liquid phase, respectively. ΔH is the melting enthalpy. This α_{shape} parameter, for a given material, depends only on the shape.

The grain size of the as-grown samples calculated from XRD analysis is around 7 nm (Fig. 3). As an estimation, we can figure the grain has a square shape with the side length of 7 nm. So the α_{shape} is about 7.5 nm. T_m is around 770 °C according to Eq. (2). This T_m corresponds with our result. Fig. 3 indicates that the melting point of the ZnO grain is around 700 °C for the grain size has a sharp increase around 700 °C. The SEM images of the samples show that the ZnO grains would melt and grow together at annealing temperature above 700 °C (Fig. 2(e) and (f)).

Photoluminescence (PL) spectra obtained from the samples are shown in Fig. 4. The PL spectra are strongly dependent on the annealing. The as-grown sample exhibits a broad blue peak around 420 nm. The intensity of the blue peaks decreases when the samples were annealed at 500 °C. But, the intensity of the blue peaks increases and the FWHM of the peak becomes smaller when the samples were annealed at 700 °C. However, samples annealed at higher temperature (T3 and T4) show three different emission bands: intensity narrow UV bands around 380 nm, blue bands around 440 nm and weak green bands around 510 nm. This interesting phenomena indicates that the samples have different emission mechanisms.

Fang et al. suggest that the blue emission centered at 430 nm corresponds to the electron transition from the level of interstitial Zn to the valence band [15]. But some authors suggest that the