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Structure and properties of ZnO films grown on Si substrates with low temperature buffer layers

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Abstract

Zinc oxide (ZnO) thin films were grown on Si (1 0 0) substrates by pulsed laser deposition (PLD) using two-step epitaxial growth method. Low temperature buffer layer (LTBL) was initially deposited in order to obtain high quality ZnO thin film; the as-deposited films were then annealed in air at 700 °C. The effects of LTBL and annealing treatment on the structural and luminescent properties of ZnO thin film were investigated. It was found that tensile strain was remarkably relaxed by employing LTBL and the band-gap redshifted, correspondingly. The shift value was larger than that calculated from band-gap theories. After annealing treatment, it was found that the annealing temperature with 700 °C has little influence on strains of ZnO films with LTBLs other than directly deposited film in our experiments. Interestingly, the different behaviors in terms of the shift of ultraviolet (UV) emission after annealing between films with and without buffer were observed, and a tentative explanation was given in this paper.

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Keywords: ZnO; PLD; Buffer layer; Photoluminescence; Blueshift; Strain

1. Introduction

ZnO is a direct band-gap of 3.37 eV semiconductor with a large binding energy of ∼60 meV at room temperature, which suggests that the electron–hole pairs are stable even at room temperature and efficient UV emission from exciton can be achieved [1,2]. Hence, ZnO thin film with *C*-axis orientation is attracting great attention for its possible applications, especially in optoelectronic applications [1,3,4]. Most of these devices require high-quality epitaxial ZnO thin films.

Silicon, one of the cheapest materials for the integration of optoelectronic devices, is a potential substrate for growth of ZnO thin film. However, the direct growth of epitaxial ZnO film on Si substrate is known as an extremely difficult task due to large tensile strain between film and substrate induced by lattice mismatch and different thermal expansion coefficients. Buffer layer and annealing are two effective methods to reduce the effects of strain. Tampo et al. [5] and Yan et al. [6] had prepared high quality ZnO films with buffer layers on sapphire and Si substrates by molecular-beam epitaxy (MBE). It had been found that a buffer layer affected the electrical properties of subsequently growth undoped ZnO film and was indispensable for the growth of films with low carrier concentrations and high mobilities [5]. However, the effects of buffer layer on structure and luminescence of ZnO film are in lack of study. In this paper, we obtained high quality ZnO film with ZnO LTBL on Si substrate by PLD and then treated in air at 700 °C for 1 h to investigate how buffer layer and annealing change the structure and further affect the properties of the final films.

2. Experiments

ZnO thin films were grown on Si (1 0 0) substrates by PLD employing a pulsed Nd:yttrium–aluminium–garnet laser (355 nm, 5 Hz, 3.8 J/cm^2). Using two-step epitaxial growth, LTBLs were grown at 200 °C for 100 and 300 s in the partial oxygen pressure of 1 Torr, the growth temperature of buffer layer is much lower than that of others. After the temperature of

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the substrate was raised to 350 °C and kept for 10 min, the films were deposited under the same condition for 30 min. The target was a 99.99% pure ceramic ZnO target. The substrate was placed at 4 cm from the target. Compared with others' optimum condition 5 cm with 10 mTorr oxygen pressure [7] and 350 mTorr [8], 1 Torr oxygen pressure, in our experiment, is relatively higher and the distance between target and substrate is relatively shorter. This is due to the pressure–distance (PD) scaling law [9]. In PLD method, a higher ambient gas pressure often requires a shorter target–substrate distance in order to obtain the film with optimum quality [7].

The as-grown ZnO films were also annealed at 700 °C for 1 h in air or in oxygen ambient. The structural properties of our samples were investigated by X-ray diffraction (XRD) with Ni-filtered Cu Kα (λ = 0.154056 nm) source. The photoluminescence was pumped by He–Cd laser operating at 325 nm at room temperature.

3. Results and discussion

3.1. The effects of buffer layer

The XRD spectra of as-deposited ZnO films without and with buffer layer deposited for 100 and 300 s (labeled as sample a, b and c) are shown in Fig. 1. It shows that a strong (0 0 2) diffraction peak is accompanied by a relatively weak (1 0 1) peak in sample a, and only one peak with (0 0 2) orientation can be detected when LTBL was used. The full width at half maximum (FWHM) of the (0 0 2) peak was narrowed from 0.3644 (sample a) to 0.2225 (sample b) and 0.2833 (sample c), which indicates the improved quality of ZnO films.

The average grain sizes of as-grown samples were calculated according to Debye–Scherrer formula,

$$D = \frac{\kappa\lambda}{\Delta 2\theta \cos\theta} \quad (1)$$

where $\Delta 2\theta$ is the FWHM of XRD yields, λ the X-ray wavelength (λ = 0.154056 nm), θ the Bragg diffraction angle and κ is the correction factor [2]. The average grain size of samples a, b and c, is 22.16, 36.27 and 28.49 nm, respectively. In spite of the same growing condition, the grain size of the final film was increased by using LTBL. One thing, we should mention here, is the grain size should not be uniform even in the same film. Hence, the calculated value can only be taken as average.

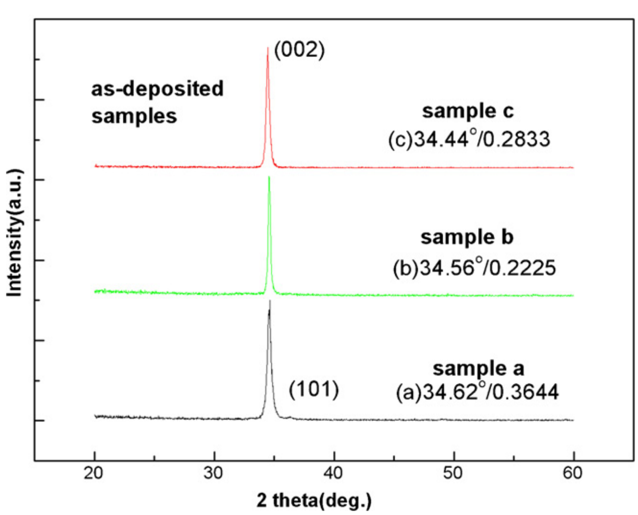

Fig. 1. The XRD patterns for as-deposited ZnO thin films of samples a, b and c.

Table 1
The position and FWHM of (0 0 2) peak, grain size and strain of as-deposited samples a, b and c

As-deposited	Sample a	Sample b	Sample c
Grain size (nm)	22.16	36.27	28.49
(0 0 2) peak position (°)	34.62	34.56	34.44
(0 0 2) FWHM	0.3644	0.2225	0.2833
Strain (GPa)	2.39	1.56	0.10

The position of (0 0 2) peak was shifted from 34.62° to 34.56°, 34.44° when applying various buffer layers. The peak of (0 0 2) orientation shifted to the value 34.43° of unstrained film [10] demonstrates the strain in ZnO films is relaxed by the LTBLs. The strain can be described by following equation due to the hexagonal symmetry of zincite [11,12],

$$\sigma_{\text{film}}^{\text{XRD}} = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \frac{c_{\text{film}} - c_0}{c_0} \quad (2)$$

where c_{ij} are the elastic constants of zincite [13] and c_0 is the strain-free lattice parameter (c_0 = 0.5205 nm measured from a ZnO powder sample [10]). The position and FWHM of (0 0 2) peak, grain size and strain of as-deposited samples a, b, c were summarized in Table 1.

Since, the sticking coefficient is large and the grown mode is amorphous at low temperature, it is relatively easy to form the nucleation of the ZnO buffer layer grown on the Si substrate [6]. It was disclosed that though the average strain was almost initially constant and relaxed slowly with the increase of thickness, the strain took a turn to the rapid strain relaxation above the layer thickness of 6–7 nm [14]. The existence of amorphous LTBL acting as transition layer is considered to confine most the dislocations generated at the interface between the substrate and the ZnO thin film. Therefore, it reduces or relaxes the effects of the oxide layer and the lattice mismatch on the quality of ZnO films. As shown in Table 1, the tensile strain can be relaxed, obviously, by employing LTBL.

The PL spectra of samples a, b and c at room temperature are shown in Fig. 2. All of our samples show strong UV band emission related to free exciton emission, and the intrinsic PL emission induced by oxygen vacancies [3,8,15,16] cannot be observed easily, which is different from the results of others [3,8,17]. It could be attributed to the relatively higher oxygen pressure during our experiments, which can effectively weaken the intensity of the DL emission due to the constrained oxygen vacancies [18,19].

The position of UV peak redshifted from about 3.288 eV (a) to 3.277 eV (b) and 3.264 eV (c) with increasing the depositing time of the buffer layer. Quantum-confinement effect is a possible explanation for the energy shift between films with and without LTBL due to their different grain sizes. Viswanatha et al. [20] have constructed a realistic tight-binding model for