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Structural, morphological and optical properties of ZnO films by thermal oxidation of ZnSe films

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ABSTRACT

In this work, zinc oxide (ZnO) thin films were synthesized by thermal oxidation of zinc selenide films in oxygen atmosphere without introducing any catalysts or additives. According to the X-ray diffraction and morphology analysis, the ZnO films were hexagonal wurtzite structure, indicating the high crystalline quality. Strong emission peak at around 370 nm (ultraviolet) and weak emission peak at 525 nm (green) were observed in the photoluminescence spectra. The dependence of photoluminescence intensity on annealing conditions was investigated in the experiment. With the increase of annealing temperature and time, the photoluminescence intensity reached a peak at 450 °C for 45 min in oxygen, which was considered to be the optimal condition.

1. Introduction

Zinc oxide (ZnO) is a technically significant member of II–VI group of semiconductors with a wide spectrum of applications. It is a direct semiconductor with the band gap of 3.37 eV and a large excitation binding energy of 60 meV at room temperature [1]. Furthermore, ZnO has diverse properties, such as non-toxic, inexpensive, piezoelectricity, chemical stability, good biocompatibility, optical absorption and emission [2]. Based on these excellent properties, it is recognized as one of the most important photonic materials in the applications, such as in solar cells [3,4], gas sensors [5], ultraviolet light detectors [6] and thin film transistors [7]. ZnO films with a perfect crystalline structure possess narrow-band intensive ultraviolet emission (380 nm) attributed to the band to band emission and noticeably less intensive wide-band green emission (500 nm) related to the deep level defects [8]. Although the mechanism of defect-related recombination process in ZnO has been intensively studied, it remains a controversial subject.

In recent years, a variety of techniques like chemical vapor deposition [9,10], sol–gel method [11], magnetron sputtering [12], molecular beam epitaxy [13], metal-organic chemical deposition [14] and pulse laser deposition [15] have been used to fabricate ZnO films. Besides, the thermal oxidation method has been proved to be an effective way to obtain ZnO films. For example, ZnO films have been prepared by thermal evaporation of ZnS films [16,17], metallic Zn [18,19] and ZnO power [20]. In addition, the impact of thermal anneal to the photoluminescence (PL) property of ZnO films have been extensively reported in other articles [19,21]. However, study on ZnO films prepared by thermal oxidation of ZnSe films is rare. For example, it was reported by Aoki et al. that ZnO films were prepared using thermal oxidation of epitaxial ZnSe films to form p-type ZnO layer [22]. But, the optimal oxidation conditions with a significance in the study of materials had not been reported.

In this paper, we fabricated ZnO films by thermal oxidation of ZnSe films without introducing any catalysts or additives, and examined the influence of the annealing parameters in oxygen (O_2). In particular, the reaction mechanism of ZnSe oxidation was investigated, as well. What's more, crystal structure, surface morphology, and optical property of the obtained ZnO films were characterized. In addition, it will provide a thought to fabricate other metal oxide films or coating by this idea, such as preparing SnO_2, CuO, Cu_2O, In_2O_3, NiO and Al_2O_3 films by oxidation of its corresponding metal, nitrides or sulfides. As is reported that SnO_2 films were prepared by SnN_x [23]and Sn films [24], and In_2O_3 films were prepared by InN thin films [25] using thermal oxidation method.

2. Experimental procedure

We first synthesized ZnSe films and then used them as precursors to form ZnO films. The ZnSe films were deposited onto a silicon substrate from ZnSe particles (99.99%) by electron beam evaporation (EBE) method at room temperature. The background pressure of the chamber was maintained at 2.0×10^{-3} Pa and the rate of growth was 0.8–1.0 Å/s. The thickness of ZnSe films was about 200 nm ultimately. Afterwards, the as-deposited ZnSe films were annealed in a tube furnace with different temperatures of 350 °C, 400 °C, 450 °C, 500 °C, and 550 °C and different

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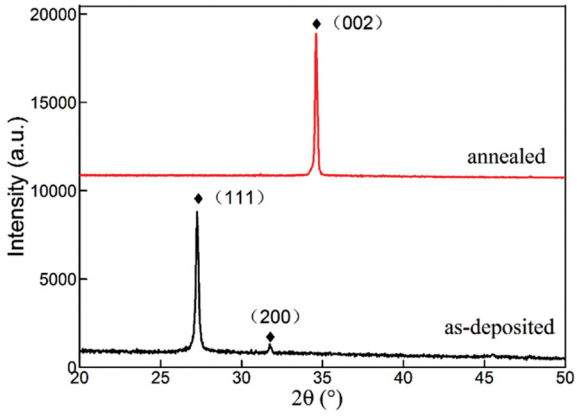

Fig. 1. XRD patterns of as-deposited and annealed films at 450 °C for 1 h.

time of 15 min, 30 min, 45 min, 60 min, and 75 min in O_2 to form ZnO films.

The nature of the crystalline phase and lattice parameters of the as-deposited and annealed films were characterized by the X-ray diffraction (XRD), with the X-ray source operated at 40 kV and 40 mA. The parallel incident X-ray beam was employed with a 0.12° roller slit at the secondary side. The measurements were performed by θ/2θ scans in the 2θ angular range of 20–50°, with a step size of 0.02° and a scan rate of 2°/min. The PL spectra were measured by an Edinburgh FLS920 spectrometer with 325 nm He-Cd laser. The surface morphologies of films were studied by scanning electron microscopy (SEM). All these measurements were carried out at room temperature.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis of samples

In order to obtain the information about the crystallographic structure, crystallinity and orientation, XRD analysis of samples was carried out as shown in Fig. 1. It shows that the diffraction peak position of the as-deposited and annealed films are different. The diffraction peaks (111) and (200) of the as-deposited ZnSe films locate at 27.3° and 31.7°, respectively, indicating the ZnSe films are cubic (zinc blende) structure (JCPDS: 80-0021) [26,27]. The diffraction peak of annealed films corresponds to (002) phase (2θ = 34.5°) of standard hexagonal wurtzite ZnO structure (JCPDS: 75-1526) [20]. No other diffraction peaks are identified in the pattern, indicating that no impurities exist in the annealed films. The average crystal size (D) of ZnSe and ZnO films is estimated by Scherrer equation [28] as follows:

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

where k = 0.89 is the Scherrer constant, λ = 0.154 nm is the X-ray wavelength of Cu-Kα, β is the full width at half maximum (FWHM) intensity and θ is the Bragg's angle of the peak. In the calculation, the intense diffraction peaks (111) of ZnSe and (002) of ZnO are chosen. The average crystal size of ZnSe and ZnO films are calculated about 78 nm and 98 nm, respectively.

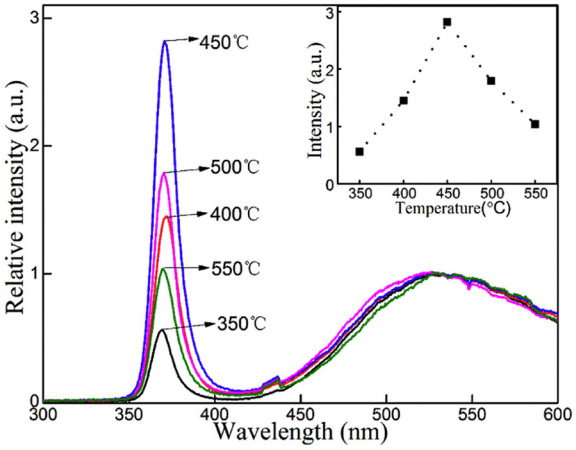

Fig. 3. PL spectra of the ZnO films annealed at 350 °C, 400 °C, 450 °C, 500 °C and 550 °C for 1 h, respectively (λ_{ex} = 325 nm). The insert figure shows the intensity trend of the photoluminescence peak at 370 nm with increasing annealing temperature.

3.2. The analysis of oxidation process

As reported, the structure of the cubic sphalerite ZnSe with the space group of F43m is similar to that of diamond [29]. Each ZnSe crystal cell contains four zinc (Zn) atoms and four selenide (Se) atoms, Zn and Se in terms of face-centered cubic close heap as tetrahedral heart each other. The lattice constant is a = b = c = 5.618 Å. For ZnO, there are three kinds of structure: hexagonal wurtzite structure, cubic sphalerite structure and rare sodium chloride type octahedral structure. As to the hexagonal wurtzite and cubic sphalerite structure, each Zn or oxygen (O) centers on its regular tetrahedron. However the hexagonal wurtzite structure has higher stability so that it is often obtained [20]. Therefore, we believe that Se atoms are replaced by O atoms with the formation of cubic sphalerite structure ZnO when the ZnSe films were annealed in O_2. Since the wurtzite structure is more stable than cubic sphalerite, the crystal structure of ZnO changed and ended up with single wurtzite ZnO in the high temperature environment. The reaction process is shown in Fig. 2. In addition, it is believed that all the Se atoms have been replaced by O atoms. Namely, only ZnO without ZnSe exists in the annealed samples. This result can also be proved by the XRD in Fig. 1.

3.3. PL of ZnO films with different annealing temperatures

Fig. 3 shows the PL spectra of the annealed films with a 325 nm excitation wavelength at room temperature. For comparison, all the data

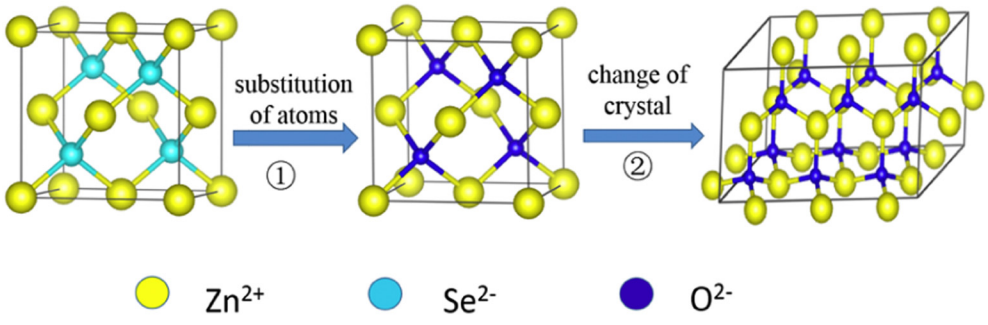

Fig. 2. Schematic diagram of oxidation process.