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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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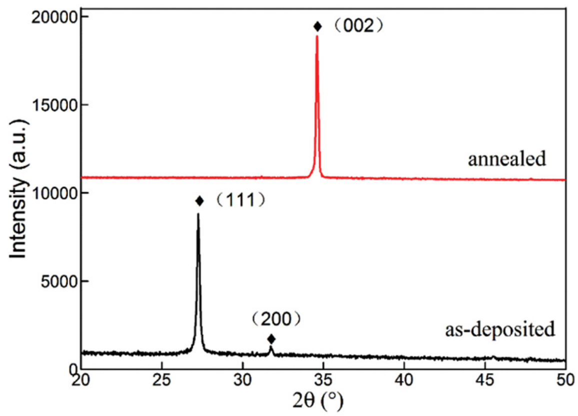

Fig. 1. XRD patterns of as-deposited and annealed films at 450 °C for 1 h.

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.

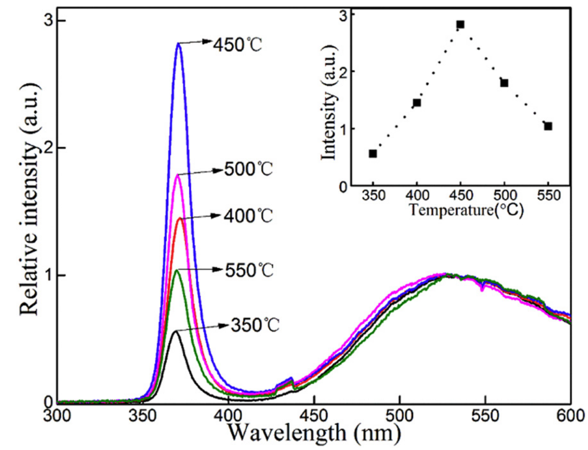

Fig. 3. PL spectra of the ZnO films annealed at 350 °C, 400 °C, 450 °C, 500 °C and 550 °C for 1 h, respectively (λ_{ex} = 325 nm). The insert figure shows the intensity trend of the photoluminescence peak at 370 nm with increasing annealing temperature.

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

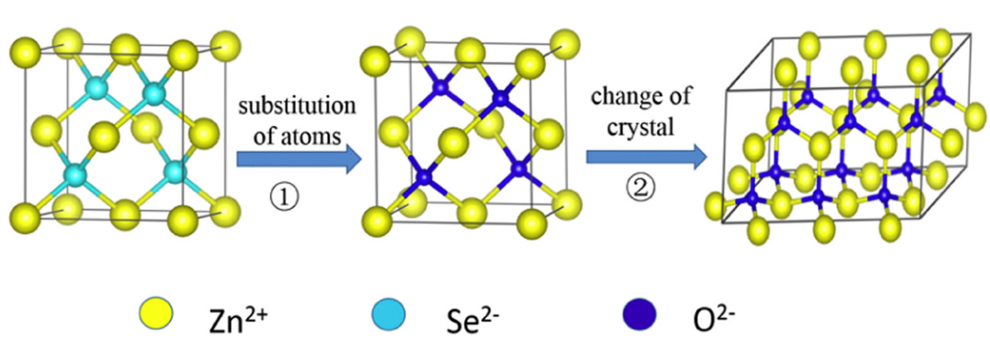

Fig. 2. Schematic diagram of oxidation process.

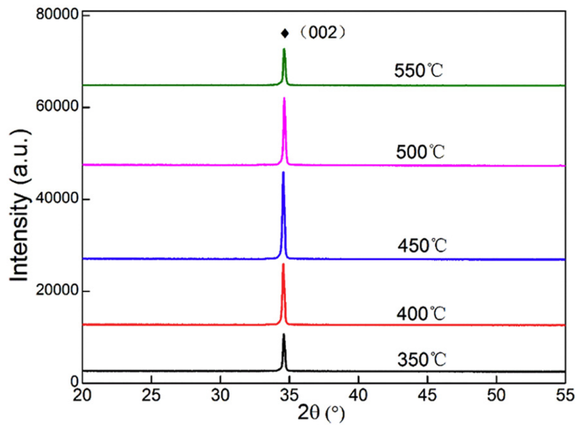

Fig. 4. XRD patterns of the ZnO films annealed at 350 °C, 400 °C, 450 °C, 500 °C and 550 °C for 1 h.

are normalized. It shows that the PL spectra are characterized by two emission bands centered at 370 nm and 525 nm, respectively. All ZnO films exhibit a sharp and strong UV emission peak dominating at the wavelength around 370 nm. As is commonly accepted, the former emission peak is typical attributed to the band to band emission due to the recombination of free excitons [1,2,7,30]. The latter one is attributed to the defect-related emission of ZnO, including oxygen vacancies, oxygen interstitials, Zn vacancies, and Zn interstitials [1,2,28,30,31]. It can be seen from Fig. 3 that no distinct shift of the shapes or positions of the emission peaks appear but the luminous intensity. The relative intensity of the 370 nm peak increases firstly and then weakens with the increase of annealing temperature, reaching to a maximum at 450 °C.

It is generally believed that the degree of crystallinity greatly has an impact on luminescence. The corresponding XRD patterns of ZnO films with different annealing temperatures are shown Fig. 4. The same location of single peak is observed. It is observed that the intensity of the crystallization peak is consistent with the conclusion as the inset of Fig. 3. Generally speaking, the annealing temperature has a decisive effect on the crystallization of the ZnO films. Crystallization is enhanced with increasing temperature, and destroyed as it become excessive. The best crystalline quality appears at 450 °C.

Typical SEM views of as-deposited and annealed films are shown in Fig. 5(a–f). These reveal that the as-deposited films have a good compactness and all the annealed films own different degrees of

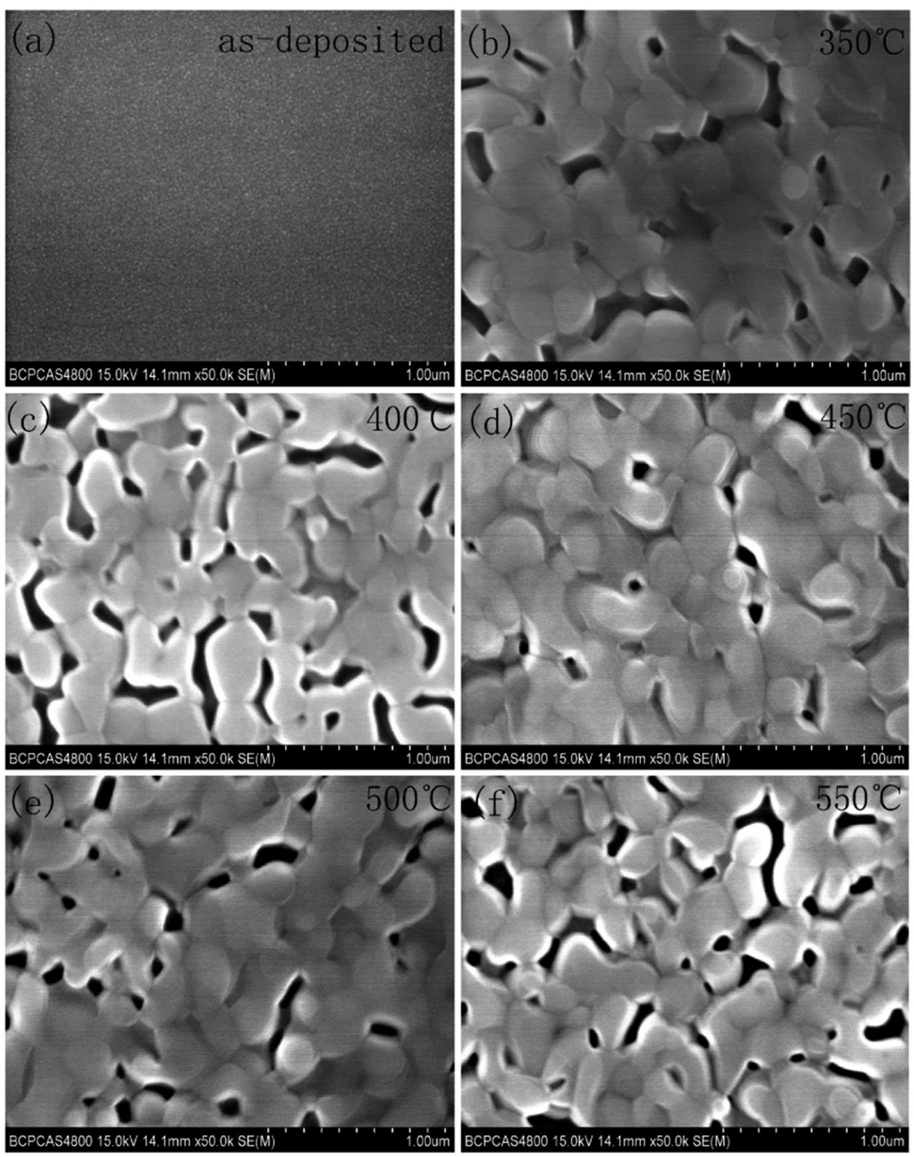

Fig. 5. Surface morphologies by SEM images of as-deposited and annealed films with various temperatures.

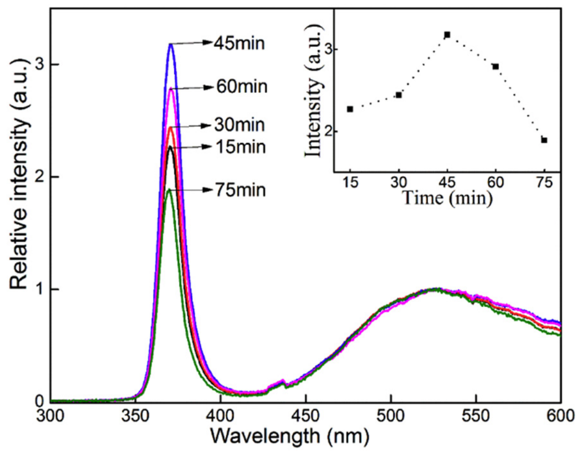

Fig. 6. PL spectra of the ZnO films annealed at 450 °C for 15 min, 30 min, 45 min, 60 min, and 75 min, respectively (λ_{ex} = 325 nm). The insert figure shows the intensity trend of the photoluminescence peak at 370 nm as a function of annealing time.

crystallization. In addition, the morphologies of the annealed films show distinctive changes. Specifically, the particles become larger as a result of the grains fusing into each other with the temperature ranging from 350 °C to 550 °C. The observed grain sizes shown in the SEM are almost identical to the estimated value with the XRD data of 450 °C.

3.4. PL of ZnO films with different annealing time

The effect of annealing time was also studied. As shown in Fig. 6, the relative intensity of peak at 370 nm increases firstly and then weakens with the extension of annealing time, which reaches a maximum at 45 min. It is generally accepted that annealing time has a direct influence on the crystallization degree of the ZnO films. The longer annealing time benefits the crystallization, and enhances the luminous intensity. However, excessive time will also destroy the crystallization, which is showed in Fig. 7. Moreover, the number of the defects will increase simultaneously with the extension of annealing time, which also strengthen the photoluminescence peak at 525 nm. Considering these two factors, the relative intensity of 370 nm emitting peak appears to be downward. We conclude that the annealing time of 45 min is the most suitable condition for obtaining a relative high photoluminescence intensity of ZnO films.

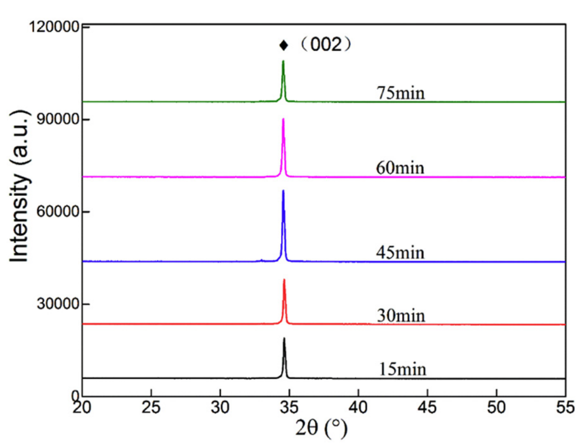

Fig. 7. XRD patterns of the ZnO films annealed with 15 min, 30 min, 45 min, 60 min, and 75 min at 450 °C.

4. Conclusion

In summary, single crystal phase ZnO thin films can be obtained by thermal oxidation of ZnSe films. All the ZnO films showed different crystalline properties with temperature ranging from 350 °C to 550 °C. The average crystal size of the annealed films at 450 °C for 1 h is about 98 nm. ZnSe thin films with cubic (zinc blende) structure are completely oxidized into ZnO with hexagonal wurtzite structure, and the reaction mechanism of ZnSe oxidation was also investigated. Meanwhile, strong emission peak of 370 nm and weak emission peak of 525 nm were observed with excitation wavelength of 325 nm, which corresponds to the band to band emission and defect-related emission, respectively. Furthermore, the process of the preparation can be precisely controlled by changing the annealing temperature and time. ZnSe films annealed at 450 °C for 45 min is considered to be the optimal condition in our experiment. The excellent optical property of the ZnO films contributes to a wide range of applications. In addition, the idea showed in this paper will provide a thought to fabricate other metal oxide films or coating in the future.

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