Structural and optical properties of ZnO thin films deposited by electron beam evaporation with different annealing temperatures

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In this work, ZnO thin films were prepared by electron beam evaporation and annealed at different annealing temperatures. The influence of annealing temperature on the structural and optical properties of the samples was studied. The structural properties of the samples were analyzed by X-ray diffraction (XRD) and atomic force microscopy. The photoluminescence was used to investigate the fluorescent properties of the samples. The results showed that the sample annealed at 300 ℃ had the best crystalline quality and optical quality. All the samples showed a strong ultraviolet emission peak and a wide green emission band. The green emission of the ZnO thin films was related to oxygen vacancy defects. With the increase of annealing temperature, the green emission increased while the ultraviolet emission gradually reduced. From the results, it is known that selecting a suitable annealing temperature is very important for obtaining high-quality ZnO thin films.
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1. Introduction

In recent years, ZnO thin films attract much attention due to their excellent optical and electrical properties such as high-transparency in the visible region, large exciton binding energy, strong ultraviolet emission, low resistivity when doped with Al, Ga and In, etc. ZnO thin films can be used in many optoelectronic devices such as solar cells [1], thin film transistors [2], light-emitting diodes [3], UV photodetectors [4], gas sensors [5], and so on. It is well known that the physical properties of ZnO thin films are sensitive to the deposition conditions and annealing treatments. Therefore, it is very important to deeply investigate the influence of deposition techniques and annealing treatments on the optical and electrical properties of ZnO thin films for their practical applications.

So far, many techniques have been used to prepare ZnO thin films. These techniques include pulsed laser deposition [6], sol-gel method [7], magnetron sputtering [8], metal-organic chemical vapor deposition [9], electron beam evaporation [10, 11], etc. Among these techniques, the electron beam evaporation has aroused many people's interest owing to some advantages such as low growth temperature, large area of the films prepared, higher purity for deposited films, strong adhesion between film and substrate, etc. Although the electron beam evaporation process is a comparatively simple technique for depositing ZnO thin films, there are still some factors that will affect the physical properties of the samples. These factors include substrate temperatures [12-14], oxygen partial pressure [15], annealing temperatures [16-18], etc. As for the influence of annealing temperature on the physical properties of ZnO thin films deposited by electron beam evaporation technique, some related studies have been performed. For example, Mahmood et al. [16] prepared ZnO thin films by reactive electron beam evaporation technique and annealed the samples at various temperatures for 2 h in air. Kim et al. [17] prepared Ag-doped ZnO thin films by electron beam evaporation and the samples were annealed for 5 h in air. Aghamalyan et al. [18] also prepared ZnO thin films by electron beam evaporation and performed a three-step annealing treatment on the samples. Undoubtedly, these studies are very helpful for us to learn more about the effect of annealing on the physical properties of ZnO thin films deposited by electron beam evaporation. However, a long annealing time or a multi-step annealing treatment [18] had been adopted in the above-mentioned studies. From the point of view of practical application, a more simple annealing treatment is a better choice. In this work, we adopted relatively low annealing temperatures (300~500 ℃) and a short annealing time (30 min) to treat the samples. The results showed that the sample annealed at 300 ℃ presented the excellent crystalline and optical quality. The effect of annealing temperature on the structural and optical properties of ZnO thin films was investigated deeply.

2. Experiments

ZnO thin films were deposited by evaporation beam evaporation equipment (PMC90S, Protech Korea Ltd.). The raw materials are high-purity (99.999%) ZnO particles. The substrate material is glass. The distance between the

substrate and evaporation source is about 1.5 m. The substrate temperature is 250 ℃. The working pressure is 3.0×10^{-2} Pa (Ar/O=1/1). The thickness of the ZnO thin films is ~150 nm. After the deposition, the as-deposited films were annealed in air at 300, 400, and 500 ℃ for 30 min.

The crystal phase and crystalline orientation of the samples were analyzed by an X-ray diffractometer (Bruker D8 Advance). The surface morphologies were studied by an atomic force microscope (CSPM4000) in contact mode. The transmittance was measured by a UV-visible spectrophotometer (Lambda 950). The photoluminescence spectra were recorded by a fluorophotometer (FluoroMax-2) with an excitation wavelength of 325 nm.

3. Results and discussion

3.1. The influence of annealing temperature on the microstructure of ZnO thin film

Fig.1 shows the XRD patterns of ZnO thin films annealed at different temperatures. All the samples present a strong diffraction peak at ~ 34.5° corresponding to the (002) peak of wurtzite-structured ZnO, which means the ZnO thin films are preferentially oriented along the c-axis perpendicular to the substrate surface. It can be seen from Fig.1 that the intensity of the (002) peak is enhanced after the films are annealed. The sample annealed at 300 ℃ shows the strongest (002) peak. However, the intensity of the (002) peak decreases again when the annealing temperature is above 300 ℃. This phenomenon is very similar to that observed by Vinodkumar et al. [6]. The full width at half maximum (FWHM) of the (002) peak is displayed in Fig.2, which largely decreases after annealing treatment. The value of the FWHM of the sample annealed at 300 ℃ is very close to that of the ZnO thin film annealed at 700 ℃ in the experiment of Mahmood et al. [16]. The reduction of the FWHM indicates that the crystallization of ZnO is enhanced. The crystallite size of ZnO thin film is estimated by Scherer formula:

$$d = \frac{0.9\lambda}{\beta\cos\theta}$$

where d is the crystallite size, λ is the wavelength of X-ray, β is the FWHM and θ is the Bragg's angle in degrees. From Fig.2, it can be seen that the crystallite size increases after the film is annealed. The sample annealed at 300 ℃ shows the biggest crystallite size. However, Mahmood et al. [16] found that the crystallite size gradually increased with the increasing annealing temperature and the sample annealed at 700 ℃ had the biggest crystallite size (33.79 nm). In fact, the crystallite size of ZnO is not only affected by the annealing temperature but also deposition conditions. For example, Vinodkumar et al. [6] prepared ZnO thin films by pulsed laser ablating a ZnO target for 10, 15 and 20 min (the resulting film is labeled as A1, A2 and A3, respectively) and studied the effect of annealing temperature on the structural and optical properties of the samples. They found that the crystallite size in A1 film annealed at 300 ℃ is 19 nm and its value changes to 22 and 14 nm when annealed at 400 and 500 ℃. As for A2 and A3 films, the crystallite size is found to increase with the increasing annealing temperature. This sentence is not very clear: For our samples, from the (002) peak intensity, FWHM and crystallite size, it can be known that the sample annealed at 300 ℃ shows the best crystalline quality and c-axis orientation. However, for our samples judging from the (002) peak intensity, FWHM and crystallite size values, the sample annealed at 300 ℃ have the best crystalline quality and c-axis orientation. These results suggest that 300 ℃ is the optimized annealing temperature for obtaining high crystalline quality ZnO thin film in our experiment. Because the deposition environment is oxygen-deficient, the prepared ZnO thin films contain some native point defects such as Zn interstitial and oxygen vacancy. When the films were annealed at 300 ℃ in air, the defects were reduced. Accordingly, the crystallization of the film was improved. However, when the annealing temperature is above 300 ℃, some defects such as oxygen vacancy increase again due to the desorption of oxygen atoms, which leads to the degradation of the crystallization. The similar results have been also reported by others [7].

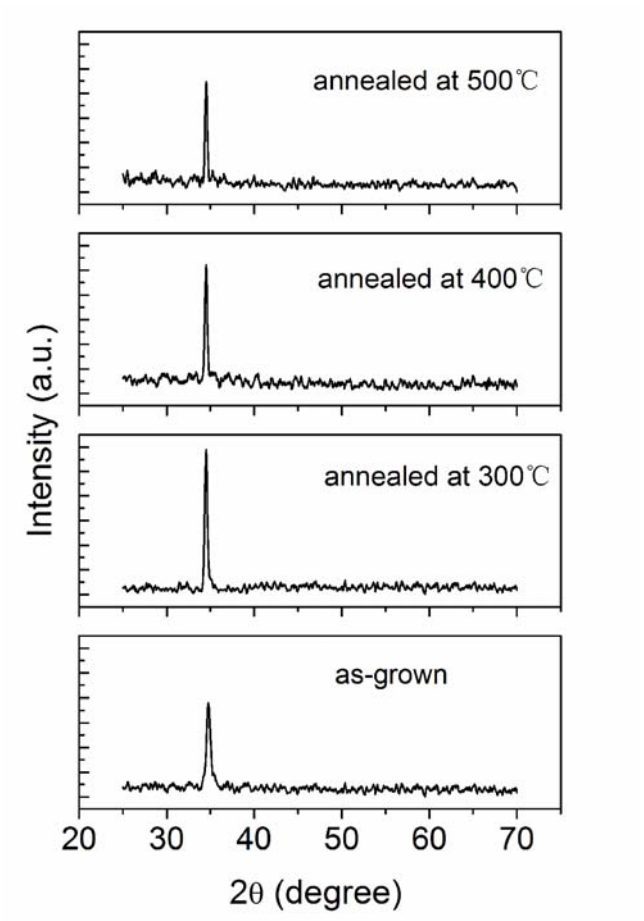

Fig.1. XRD patterns of ZnO thin films

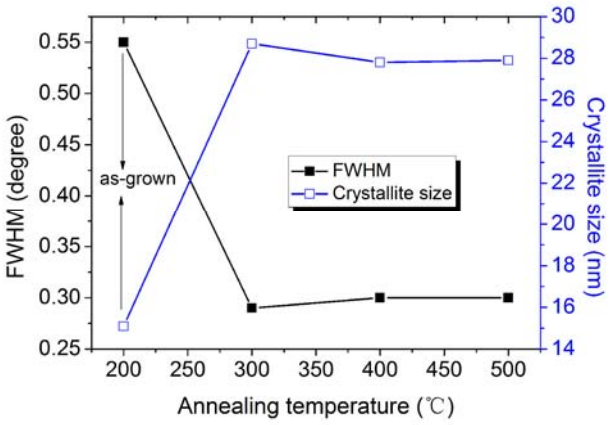

Fig.2 Variation of the FWHM and crystallite size as a function of annealing temperature

Fig.3 presents the surface morphology images of the ZnO thin films. It can be seen that all the samples become denser after annealing treatment. However, the average surface roughness is increased with the increase of annealing temperature as shown in Fig.4. The sample annealed at 300 ℃ has the smoothest surface and the most uniform grain size. When the annealing temperature is above 300 ℃, the grains become nonuniform and surface roughness is also increased. It is clear that the grains in the plane have a triangular shape, while it is often observed that ZnO grains have a round shape in the plane. The different surface morphology mainly results from different deposition conditions and annealing treatments.

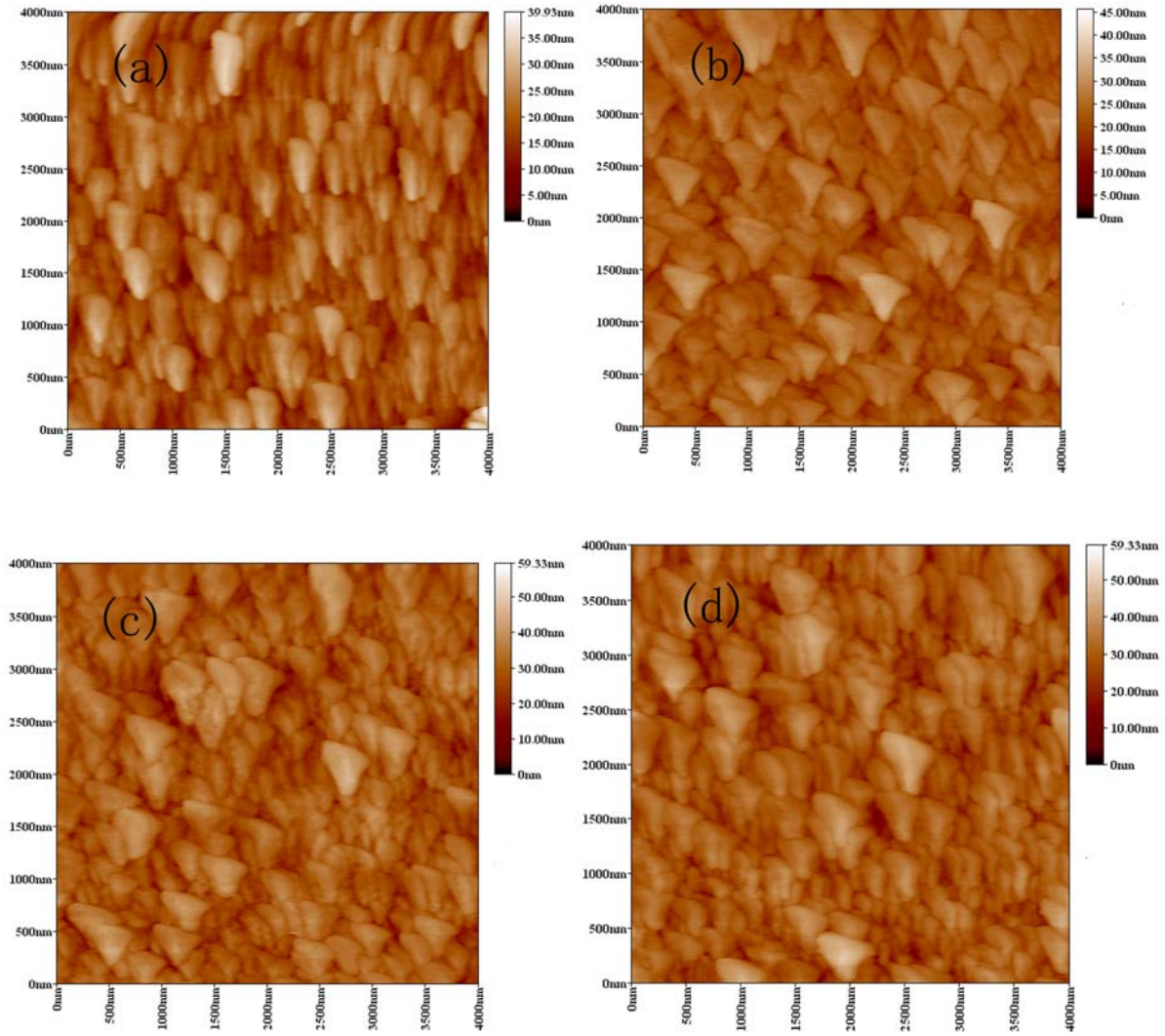

Fig.3 Surface morphology images of the as-deposited ZnO thin film (a) and ZnO thin films annealed at 300℃ (b) , 400℃ (c) and 500℃ (d)

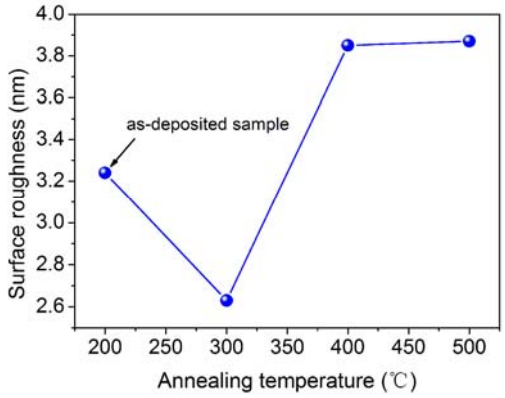

Fig.4 Surface roughness of the samples

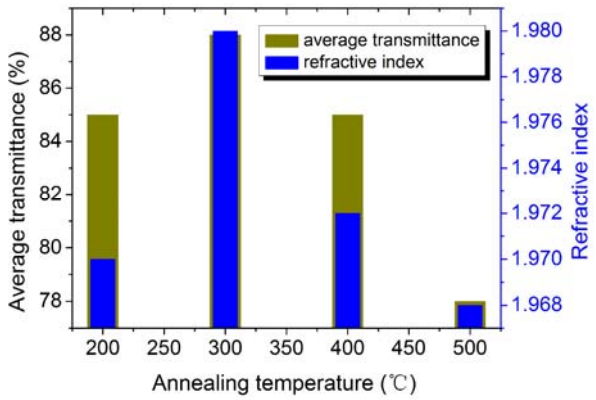

Fig.6 Average transmittance and refractive indexes of the samples

3.2. The influence of annealing temperature on the optical properties of ZnO thin films

Fig.5 displays the transmittance spectra of the samples. All the samples exhibit high transparency in the visible region. Therefore, these films can be used as transparent window materials for some optoelectronic devices. Fig.6 gives the average transmittance in the visible range. As for the sample annealed at 300 ℃, it shows the highest transmittance in the wavelength range from 400 to 800 nm. This is probably connected with the following two factors: (1) the sample annealed at 300 ℃ has the best crystalline quality and the most uniform grains, which can increase the transmittance; (2) this sample has the minimum surface roughness, which maybe probably decreases the light scattering on the surface. The sample annealed at 500 ℃ displays the lowest transmittance in the visible region, which is mainly ascribed to the increased surface roughness. The refractive indexes of the samples have been measured by an ellipsometer (the working wavelength λ=632.8 nm), as are shown in Fig.6. The refractive index of the sample annealed at 300 ℃ is the highest and it is close to that of bulk ZnO (n=2.0). This indicates that the quality of crystallization of this film is very good. However, the refractive index again decreases when for the annealing temperature is above 300 ℃. The similar phenomenon was is also observed by others [7]. It is probably caused by the degradation, the roughness increase for instance, of the film crystallization of the film when the annealing temperature is above 300 ℃.

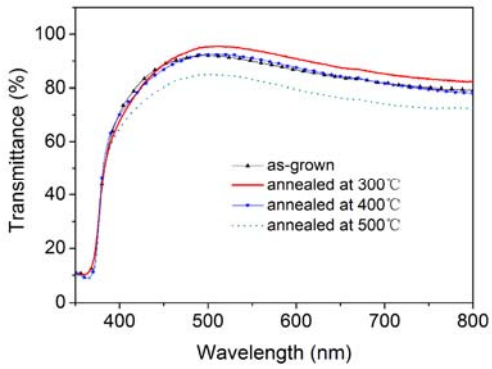

Fig.5 Transmittance spectra of the samples

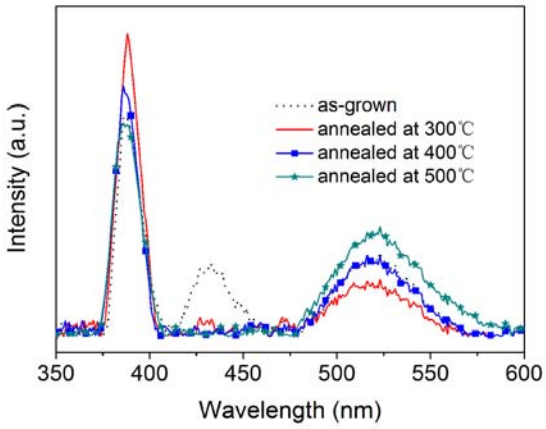

Fig.7 Photoluminescence spectra of the samples at room temperature

Fig.7 shows the room-temperature photoluminescence spectra of the samples. All the samples present a strong ultraviolet (UV) emission peak and a wide green emission band. For the as-deposited sample, besides the UV and green emission, it also has a violet emission peak located at 434 nm was observed. The UV emission is generally attributed to the recombination of free excitons [7, 9]. The intensity of UV emission is mostly related to the crystalline quality of the films. It is clear from Fig.7 that the sample annealed at 300 ℃ shows the strongest UV emission. This indicates that the crystalline quality of the ZnO thin film is largely improved after it is annealed at 300 ℃. As a result, the density of free excitons are greatly increased, leading to the stronger UV emission. However, when the annealing temperature is further enhanced, the UV emission is reduced in turn. This is probably due to the decline worsening of in crystalline quality of ZnO thin films when the annealing temperature is beyond 300 ℃. What is More interesting is that the green emission is gradually enhanced with the increase of annealing temperature. The similar phenomenon also occurred in ZnO thin films studied deposited by Sharma et al. [7]. Sharma et al. found that the ZnO thin film annealed at 400 ℃ presented the strongest UV emission and the lowest green emission, while the UV emission was

reduced and the green emission was enhanced as the annealing temperature was beyond 400 ℃. Although the green emission has been observed in all kinds of ZnO materials, its emission mechanism is unclear as yet. Many researchers deem that the green emission is mainly connected with oxygen vacancy defects [7, 9]. For our samples, We also ascribe the green emission of our samples to oxygen vacancy defects for following reasons:, (i) The films were deposited in an oxygen-deficient environment. (ii) as far as the annealing temperature is increased, some oxygen atoms on the film surface could be desorbed and consequently All these factors can result into formation of oxygen vacancies in the films. With respect to the violet emission centered at 434 nm, we suppose it is possibly related to the zinc interstitial defects [9]. With the increase of annealing temperature, the density of zinc interstitials are decreased and accordingly, the violet emission also is reduced.

Form the above optical analyses, it can be known that the ZnO thin film annealed at 300 ℃ has the best optical quality.

4. Conclusion

In this work, ZnO thin films were prepared by electron beam evaporation. The influence of annealing temperature on the structural and optical properties of these films was studied deeply. The results showed that the film annealed at 300 ℃ had the best crystalline quality and optical quality. When the annealing temperature was above 300 ℃, the UV emission decreased and the green emission increased. The green emission is suggested to be probably connected with oxygen vacancy defects.

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