Photoluminescence and excitonic absorption of ZnO/SiO_2 multilayer thin films under various annealing temperatures

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SiO_2 has an important regulation effect on the luminescence of ZnO nanomaterials. In this study, the ZnO/SiO_2 multilayer thin films were prepared by electron beam evaporation and the influence of various annealing temperatures on optical properties of the samples was investigated. The X-ray diffraction (XRD) patterns show that all the samples exhibit a (002) peak of wurtzite ZnO. With the increase of annealing temperature, the intensity of the (002) peak is increased and its full width at half maximum (FWHM) is decreased, which means the crystalline quality of ZnO is gradually improved. Compared with the pure ZnO thin films with the same annealing temperatures, the ZnO/SiO_2 multilayer thin films have much smoother surfaces. The absorption spectra display that the excitonic peak is more obvious and the absorption edge becomes much sharper and steeper after annealing treatments. This suggests that the defect density in ZnO layers is reduced. With the rise of annealing temperature, the ultraviolet emission of ZnO is evidently enhanced, which can be attributed to the increased density of free excitons. On the other hand, the ultraviolet emission peak has a slight blue-shift with the increasing annealing temperature, which is probably connected with the improvement of the crystalline quality and the decrease of defect density in ZnO grains.

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1. Introduction

In recent years, semiconductor materials with wide bandgaps like GaN, ZnS, SiC, and ZnO, have attracted lots of attention in the world. Compared with other semiconductors, ZnO has some obvious advantages such as non-toxicity, abundant raw materials, low-temperature epitaxial growth, large excitonic binding energy (~60 meV), excellent optical and electrical properties, etc. These characteristics make ZnO thin films have many promising applications in optoelectronic devices such as light-emitting devices [1,2], thin film transistors [3,4], ultraviolet photoconductive detectors [5,6], optical waveguides [7,8], etc. In order to obtain better optical properties and develop a wider range of applications of ZnO thin films, many researchers carried out doping for ZnO with other elements [9,10] or prepared ZnO-based composites by utilizing other materials to modify ZnO [11-16]. Among these, utilizing metal oxides to adjust optical properties of ZnO materials is very attractive. For example, Yang et al. [17] fabricated transparent ZnO-SiO_2/silicone nano-composites which showed tunable emission colors when the ratio of ZnO to SiO_2 was adjusted. Caglar et al. [18] prepared ZnO/CuO composite thin films and those films exhibit tunable optical and electrical properties when the Cu content increased from 1% to 100% in the films. Babu et al. [19] prepared ZnO/mesoporous silica nanocomposite and studied the influence of the precursor, annealing temperature, surface area and excitation wavelength on photoluminescence of the samples. They found that the emission intensity was enhanced with the rise of the surface area of the host and thought that it may be due to the enhancement in the density of Zn-O-Si bonds with the increase in surface area. This evidently indicates the important effect of silica on the luminescence of ZnO. Hagura et al. [20] also found that the silica nanoparticle size and SiO_2-to-ZnO concentration ratio had a great effect on photoluminescence of ZnO nanoparticles. In regard to the ZnO/SiO_2 composite materials, many ZnO/SiO_2 composite nanoparticles were prepared and investigated, but ZnO/SiO_2 composite thin films with multilayer structures are seldom reported as yet.

In one study of our group [21], we prepared ZnO/SiO_2

composite thin films and investigated the effect of the thickness of SiO_2 interlayers on the optical properties of ZnO thin films. It is found that the transmittance of ZnO thin films is improved and the ultraviolet (UV) emission is enhanced due to the introduction of SiO_2 interlayers. Especially, when the thickness of SiO_2 interlayers is 4 nm, the composite film presents the strongest UV emission. In this work, in order to know the change of the optical properties by various annealing temperatures, we performed annealing treatment at various temperatures for the samples with SiO_2 interlayers of 4 nm thickness. It is found that the UV emission intensity, the position of UV peak and the excitonic absorption have been much changed after annealing treatments. The details are discussed below.

2. Experiments

ZnO/SiO_2 composite films with a mutilayered structure were deposited by electron beam evaporation equipments (PMC90S, Protech Korea Ltd.). The preparation process and deposition parameters have been described elsewhere [21], thereby not repeatedly narrated here. A layer of ZnO and a layer of SiO_2 form a unit; each composite film includes four units. The raw materials of the composite films are high-purity ZnO and SiO_2 particles. In order to study the influence of annealing temperature on the ZnO/SiO_2 composite films, four identical samples have been prepared in which the thickness of SiO_2 interlayers is 4 nm. Three of the samples were annealed at 300, 400 and 500 ℃ in air for 0.5 hour and correspondingly are labeled as sample B, C and D, respectively. The as-deposited one is labeled as sample A. Considering that the ordinary glass substrate will be deformed when the annealing temperature is above 500 ℃, we do not annealed the samples at higher temperatures.

The cross-section morphology of the multilayer thin film was observed by a field emission scanning electron microscope (S4800). The crystal phase and crystalline orientation of the samples were analyzed by an X-ray diffractometer (D/max-2500/PC). The transmittance and absorption spectra were recorded by a spectrophotometer (UV-3600). The photoluminescence of the composite films was investigated by a PL spectrometer (LS50B) with an excitation wavelength of 325 nm at room temperature.

3. Results and discussion

3.1 Structural properties of ZnO/SiO_2 multilayer films annealed at different temperatures

Fig. 1 (a) shows the cross-sectional morphology image of the ZnO/SiO_2 composite thin film annealed at 300 ℃, from which we can clearly see that the film is composed of multilayer of ZnO and SiO_2. The thickness of each layer is very uniform and the structure is very compact. The ZnO layers include many columnar grains, while the SiO_2 layers show no obvious grains. It should be noted that there is no obvious difference to be observed in the cross-sectional morphologies of the four samples due to the limited resolution of the SEM. Therefore, other morphological images of the samples are not given here. Fig. 1 (b) shows the cross-sectional morphology of the pure ZnO thin film annealed at 300 ℃. Compared with the pure ZnO thin films annealed at the same temperature, the ZnO/SiO_2 multilayer thin films show much smoother surface. As for the pure ZnO thin films, many results show that ZnO grains will grow up when ZnO thin films are annealed at relatively high temperatures, leading to the surface roughness to increase rapidly. It is known that the rough surface of the thin films is unfavorable for some applications. However, with the same anneal temperature, the ZnO/SiO_2 multilayer thin films present much smoother surface. This may be because the SiO_2 interlayers inhibited the excessive growth of ZnO grains.

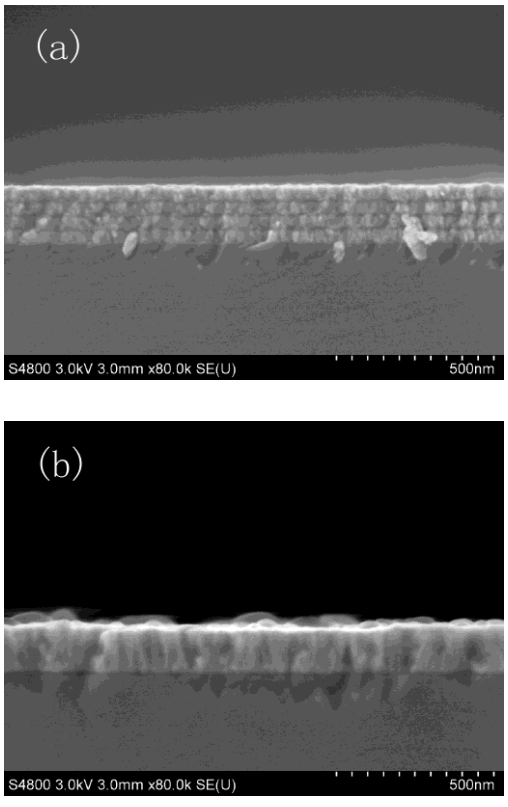

Fig. 1. Cross-sectional morphology images of the ZnO/SiO_2 composite film (a) and the pure ZnO thin film (b).

Fig. 2 gives the XRD patterns of the ZnO/SiO_2 multilayer films annealed at various temperatures. All the samples show a strong (002) peak of ZnO, which means the ZnO is crystallized in a wurtzite phase and has a

preferred orientation along the c-axis, while the SiO_2 layers are amorphous. With the increase of annealing temperature, the intensity of the (002) peak of ZnO is gradually enhanced while the FWHM is gradually decreased, which suggests that the crystalline quality of ZnO is gradually improved. The similar results have been observed in many studies [22,23]. According to the Scherrer formula:

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

Where d is the crystallite size of ZnO, λ is the wavelength of X-ray, β is the FWHM of the (002) peak and θ is the diffraction angle, we obtained the crystallite size of ZnO of the samples and the values are 16.2, 17.3, 19.0 and 20.7 nm, respectively, for sample A, B, C and D. With the rise of annealing temperature, the ZnO crystallite size is increased gradually. This is because annealing supplies ZnO with enough energy to make coalescence occur in ZnO layers.

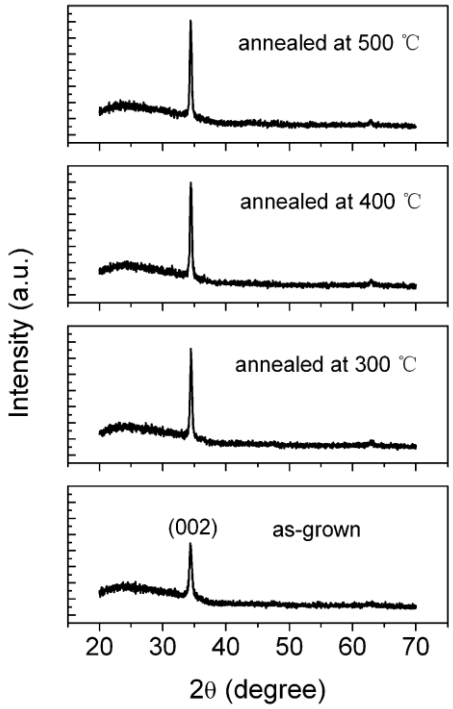

Fig. 2. XRD patterns of the samples.

3.2 Optical properties of ZnO/SiO_2 multilayer films annealed at various temperatures

Fig. 3 displays the transmittance spectra of the composite thin films. In the visible and near-infrared region, all the ZnO/SiO_2 multilayer thin films show high transmittance. The average of the transmittance is above 90%. However, a sharp and steep absorption edge is observed at 370 nm or so. The composite films show a strong absorption in the UV region. Fig. 4(a) gives the absorption spectra of the samples from which it can also be seen that the composite films possess a strong absorption performance in the UV region. The spectra of the ZnO/SiO_2 multilayer films show clearer exciton absorption peaks after annealing treatment. The inset in Fig. 4 (a) is the amplified excitonic peaks centered at 361 nm. In general, the excitonic absorption is closely related with the crystalline quality of ZnO. The higher the crystalline quality and the less the structural defects is, the stronger the excitonic absorption is. That the annealed samples show clearer excitonic absorption peaks indicate the improvement of the crystalline quality and the decrease of structural defects of ZnO. This is well in agreement with the results from XRD analysis. The absorption spectra of ZnO at low temperatures usually show three excitonic peaks [24], which can be labeled as exciton A, B and C, respectively, according to the ascending order of energy. At room temperature, however, one can only see the exciton A. The absorption spectra at room temperature can be divided into three regions as shown in Fig. 4 (b). According to the explanation of Liu and Chua [25], in region Ⅰ, the absorption is caused by defects or impurities in the ZnO crystal; the absorption in region Ⅱ is due to the exponential tail of the density of exciton localization states and the strong absorption in region Ⅲ is assigned to the intrinsic exciton absorptions. In comparison with the unannealed sample, the absorption edges of the annealed ones are much steeper and the absorption in region Ⅰ is less. This can be ascribed to the improvement of crystallization and the decrease of structural defects.

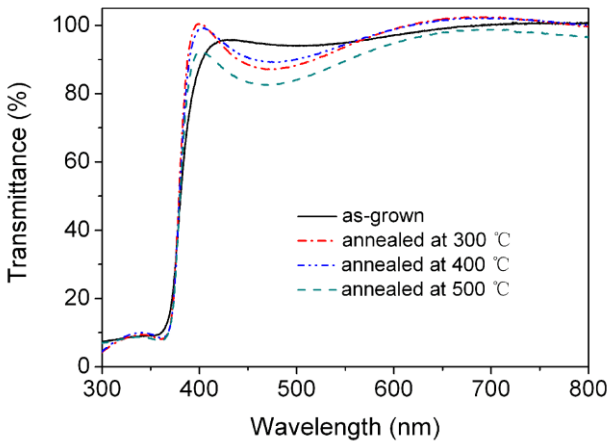

Fig. 3. Transmittance spectra of the samples.

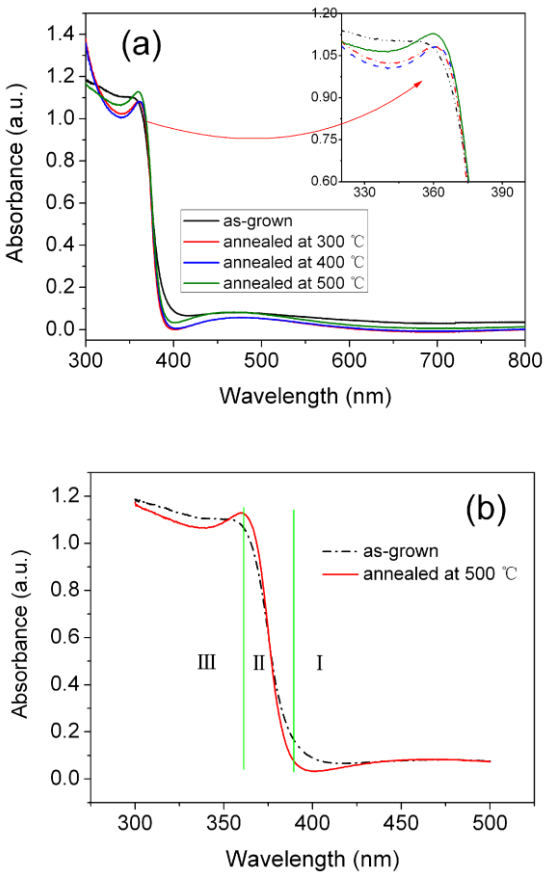

Fig. 4. Absorption spectra of the samples (a) and (b).

Fig. 5 shows the room - temperature photoluminescence spectra of ZnO/SiO_2 multilayer thin films annealed at various temperatures. All the samples exhibit a strong near-band-edge emission which is generally attributed to the recombination of free excitons. The annealing treatment caused two changes for the UV emission. On the one hand, the intensity of UV peaks is enhanced gradually with the increase of annealing temperature; on the other hand, the UV emission peak has a blue-shift after annealing treatment. The enhancement of the UV emission mainly results from the increase of the density of free excitons. However, the shift of the UV emission peak is relatively complicated. As for the UV emission peak of ZnO, some researchers found that it had a blue-shift with the rise of annealing temperature. For example, Sagar et al. [26] observed that the UV emission peak shifted from 389.5 nm to 380.8 nm when the annealing temperature was increased from 300 to 600 ℃. They thought that the shift of UV peak was probably connected with the variation of the stress in the films. Hong et al. [27] also observed the blue-shift of the UV peak. However, other researchers found that the UV peak had a red-shift with the increase of annealing temperature. For instance, Li et al. [28] found that the UV emission peak of ZnO thin films prepared by sol-gel method had a red-shift with the enhancement of the annealing temperature. They thought that some new defects such as oxygen vacancies and Zn interstitials may be produced in the films at higher annealing temperatures, thus leading to a red-shift of the UV peak. As for our samples, from the above analyses of XRD and excitonic absorption, we can know that the crystalline quality of ZnO is improved and structural defects are reduced with the increase of annealing temperature. Therefore, we think that the blue-shift of UV emission peak can be attributed to the improvement of crystallization and the decrease of structural defects.

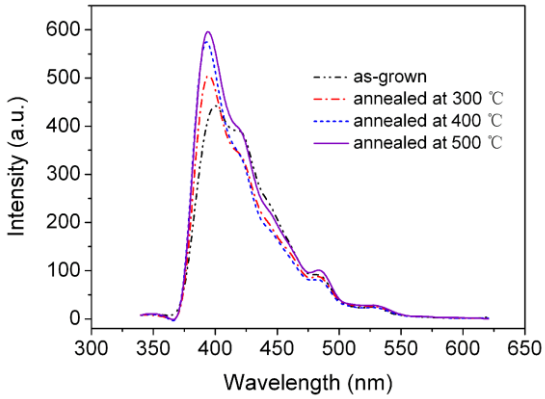

Fig. 5. Photoluminescence spectra of the samples.

4. Conclusion

In this work, we investigated the evolution behavior of structural and optical properties of ZnO/SiO_2 multilayer films with different annealing temperatures. The results show that the ZnO/SiO_2 multilayer films exhibit much smoother surface than the pure ZnO thin films annealed at the same temperatures. All the samples show high transmittance in the visible region. With the rise of annealing temperature, the crystallization of ZnO is improved and the UV emission is enhanced while the visible emissions especially the green emission are little changed. Our previous study has found that the SiO_2 interlayers with a thickness from 4 to 16 nm can improve the UV emission of ZnO; this study demonstrates that the suitable annealing treatment can further improve the UV emissions. The ZnO/SiO_2 multilayer films have potential applications in light-emitting devices or flat panel displays.

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