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EFFECT OF SUBSTRATE TEMPERATURE ON THE MICROSTRUCTURE AND OPTICAL PROPERTIES OF ZnO NANOCRYSTALLINE THIN FILMS

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In this work, ZnO nanocrystalline thin films were prepared by sol–gel dip-coating method on glass substrates and the effect of substrate temperature on the microstructure and optical properties of these films was investigated. The structural properties were analyzed by X-ray diffraction (XRD) and scanning probe microscope. The optical properties were studied by UV-visible spectrophotometer and fluorophotometer. The experimental results showed that if substrate temperature was relatively high, once the substrate was dipped into ZnO sol, some aggregated colloidal particles would be absorbed on it. After the ZnO gel film was annealed, the poor quality ZnO thin film was formed, which had a weak ultraviolet emission and a relatively strong defect-related visible emission.

Keywords: ZnO nanocrystalline thin films; sol–gel method; substrate temperature; crystalline quality; optical properties.

1. Introduction

ZnO, an important wide band gap semiconductor ($E_g = 3.37$ eV at room temperature[1]) with a large exciton binding energy of 60 meV, can produce exciton emission at room temperature or higher temperature. Therefore, it is an ideal material for fabrication of short-wavelength optoelectronic devices. Due to its high refractive index and chemical stability, ZnO is also an appropriate material for the fabrication of photonic crystals.[2,3] So far, ZnO has been studied mainly in the form of thin films. ZnO thin film is a transparent conductive thin film. It can be applied in optical waveguides,[4] ultraviolet light-emitting diodes,[5] ultraviolet lasers,[6] ultraviolet photoconductive detectors,[7] thin film transistors,[8] optical memories[9] and so on.

Up to now, ZnO thin films have been prepared by various techniques, such as pulsed laser deposition,[10,11] magnetron sputtering,[12,13] molecular beam epitaxy,[14,15] sol–gel method,[16,17] etc. In these techniques, sol–gel dip-coating method has been receiving much attention due to its many advantages such as simple equipment, easier composition control, low cost, better homogeneity, and easier fabrication of large

area films. However, in the sol–gel process, many factors, such as sol concentration, sol aging time, sol PH value, the kind of substrate, annealing treatment and so on, all affect the quality of the prepared films. Many researchers have studied the effects of the above-mentioned factors on the structural, optical and electrical properties of ZnO thin films, but, to our knowledge, the effect of substrate temperature on the structural and optical properties of ZnO thin films prepared by the sol–gel dip-coating method has not been reported yet. It is well-known to all that every time the substrate is coated with ZnO sol, it must be dried and given a pre-heat treatment in the sol–gel method. After the pre-heat treatment, the substrate coated with ZnO gel film will remain a certain temperature. This temperature will affect the quality of ZnO thin films prepared by the sol–gel dip-coating method. Since the sol–gel dip-coating method is a promising technique for fabrication of large-area films, thus it is important to study how to improve the sol–gel dip-coating process for obtaining good quality ZnO thin films and high preparation efficiency. In this work, ZnO thin films were prepared by the sol–gel dip-coating method and the effect of substrate temperature on the structural and optical properties of the films was investigated.

2. Experiments

Zinc acetate dehydrate $(Zn(CH_3COO)_2 \cdot 2H_2O)$, ethanol, monoethanolamine (MEA) were used as a starting material, solvent, sol stabilizer, respectively. Zinc acetate was first dissolved in ethanol at room temperature. Then the resulting mixture was stirred at $60°C$ for an hour. When the mixture was stirred, MEA was put into it drop by drop. The molar ratio of MEA and zinc acetate was maintained 1.0. Finally, a clear and transparent homogenous sol was formed. The concentration of zinc acetate was $0.3 \, mol/L$. The ZnO sol was aged for 24 hours at room temperature and then ZnO thin films were prepared by the sol–gel dip-coating method on glass substrates which had been cleaned and dried. Every time the substrate was withdrawn from the ZnO sol, it was put into a furnace to be dried and given a pre-heat treatment at $380°C$ for 5 minutes. The procedure from dip-coating to drying was repeated six times. At last, the ZnO thin film was annealed at $500°C$ in air for an hour. Altogether three samples were prepared. These three samples were different in the dip-coating process. For the first sample (labeled A), after the substrate coated with ZnO gel film had been given a pre-heat treatment, the next dip-coating did not start until it was cooled down to room temperature. For the second sample (labeled B), the next dip-coating did not start until it was cooled down to $90°C$. For the third sample (labeled C), the next dip-coating did not start until it was cooled down to $130°C$.

The crystal phase and crystalline orientation of the samples were analyzed by an X-ray diffractometer (Bruker D8 Advance). The surface morphologies were observed by a scanning probe microscope (CSPM4000). The transmittance and photoluminescence were measured by a UV-visible spectrophotometer (Lambda 950) and fluorophotometer, respectively. The excitation source was a Xe lamp; the excitation

wavelength was 325 nm. All the measurements were carried out at room temperature in air.

3. Results and Discussion

3.1. *Structural properties of the prepared ZnO thin films*

Figure 1 shows XRD patterns of the prepared ZnO thin films. For sample A, its (002) diffraction peak is high and the full-width at half-maximum (FWHM) of the (002) peak is small. This suggests that the crystalline quality of sample A is very good. Except for the (002) peak, there is no other peak in the pattern of sample A. Regarding sample B, its (002) peak is predominant, but the intensity of the (102) peak is obviously getting strong. Regarding sample C, its (102) peak is almost as high as the (002) peak, and the (100) and (110) peaks occurred. The above results indicate that all the samples are hexagonal wurtzite structure. Sample A and sample B are preferentially oriented along the *c*-axis perpendicular to the substrate, but sample C does not show a preferential growth orientation. According to the order of samples A, B, and C, the intensity of their (002) peaks declines in sequence but the FWHM gradually increases. This means that the quality of the films gradually falls off. The average crystallite sizes of the samples can be calculated with the Scherrer formula[18] using parameters derived from XRD patterns. The average sizes are 24.7 nm, 23.4 nm and 21.3 nm for samples A, B, and C, respectively.
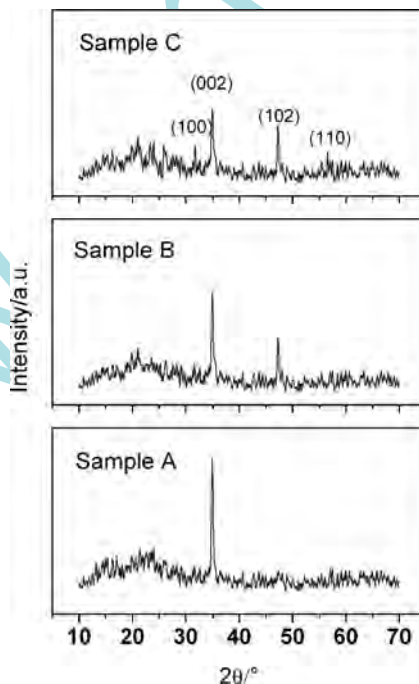

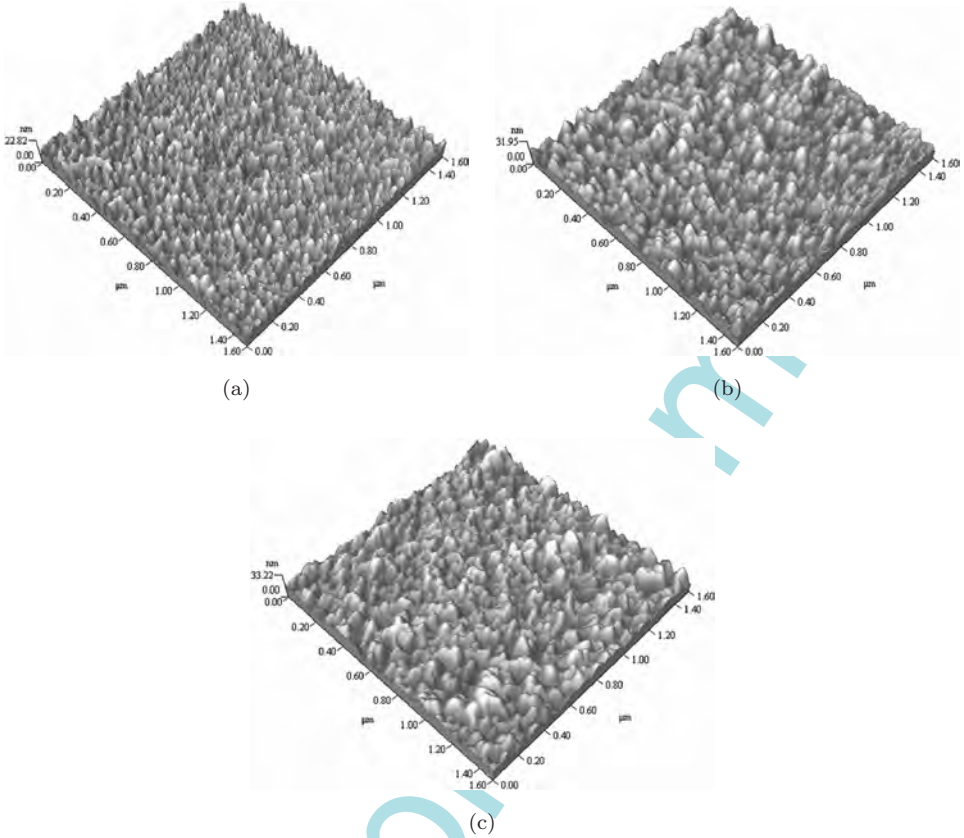Fig. 1. XRD patterns of the prepared ZnO thin films.

(a)

(b)

(c)

Fig. 2.   Surface morphologies of (a) sample A, (b) B, and (c) C.

Figure 2 shows the surface morphologies of the samples. From Fig. 2(a), it can be seen that the surface of sample A is covered with dense columnar ZnO grains. The grain sizes are uniform. The grains grow along the *c*-axis perpendicular to the substrate, which is in agreement with the XRD analysis. The average surface roughness of sample A is 2.56 nm, so it is very smooth. It is clear from Fig. 2(b) that the surface of sample B is also covered with columnar ZnO grains, but the grain sizes are not uniform. Some grains which seem to contain several normal grains are much bigger than others. The average surface roughness of sample B is 2.71 nm. For sample C, the grain sizes are more non-uniform. Its grains grow not only along the *c*-axis orientation but also other orientations. This agrees with the XRD analysis that sample C is randomly oriented. In comparison with samples A and B, the average roughness of sample C increased to 3.01 nm.

By the above structural analysis, it can be concluded that the crystalline quality of sample A is the best. The crystalline quality of samples B and C decline to different degrees compared with sample A. This shows that substrate temperature has an effect on the crystalline quality of ZnO thin films prepared by the sol–gel

dip-coating method. If the substrate has a relatively high temperature, once it is dipped into ZnO sol, the colloidal particles around the substrate will move more intensely. The intense thermal motion of particles will result in some particles being aggregated into a bigger colloidal particle. When the substrate is withdrawn from the ZnO sol, some big particles will be absorbed on it. After pre-heat treatment, the big particles will form some heave spots on the substrate. It is easier for these heave spots to absorb ZnO colloidal particles than other spots on the substrate. Therefore, this leads to some grains growing bigger and bigger. Due to the non-uniformity of nucleation and growth of the ZnO phase, the grain sizes in the film are non-uniform, and the shape of the grains is no more a regular columnar shape. As a result, the surface roughness of the film also increases. The bigger the temperature difference between substrate and ZnO sol is, the worse the quality of the ZnO thin film prepared by dip-coating process is.

3.2. *Optical properties of the prepared ZnO thin films*

Figure 3 shows the transmittance spectra of the three samples. From Fig. 3, it can be seen that sample A has a high transmittance in the visible region. The average value of transmittance in the range from 400 to 760 nm is 90%. The absorption edge is sharp. As for sample B, its transmittance has decreased a little in the range from 380 to 600 nm. Compared with sample B, the transmittance of sample C reduced more. The transmittance is closely connected to the crystalline quality and surface roughness of the ZnO thin film. The better the crystalline quality is, the higher the transmittance is. The smaller the surface roughness is, the higher the transmittance is. From the analyses of XRD and surface morphologies, it is known that sample A has the best crystalline quality and the smoothest surface. Therefore, that sample A has the highest transmittance is in agreement with the
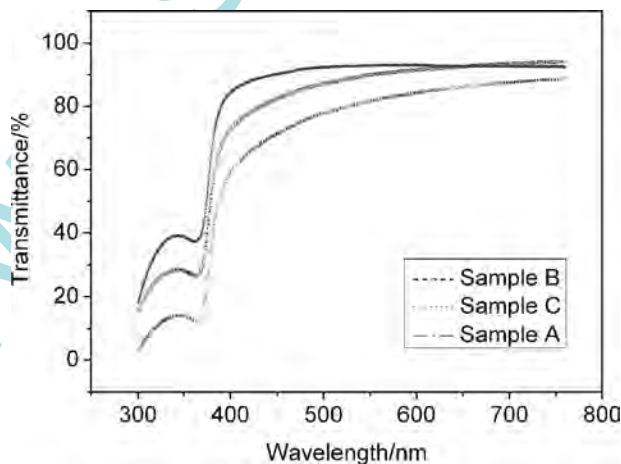

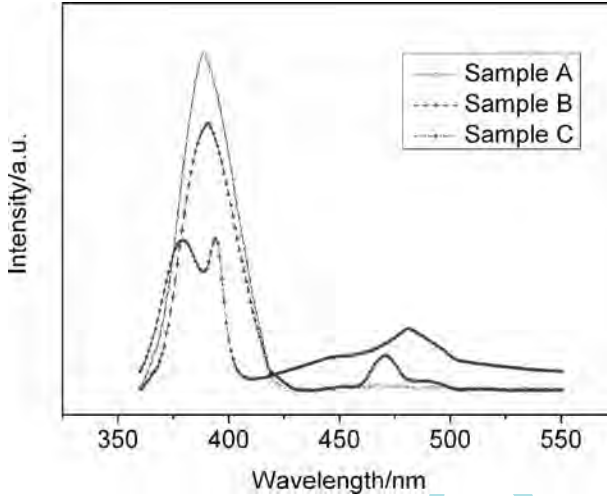Fig. 3.   Transmittance spectra of the prepared ZnO thin films.

Fig. 4.   Photoluminescence spectra of the prepared ZnO thin films.

results of XRD and surface morphologies. According to the order of samples A, B, and C, their absorption edges shift toward long wavelength. That is to say, a red-shift of absorption edges occurred. The red-shift of absorption edges is related to many factors such as doping, grain sizes, crystalline quality of the films and so on. Here, we think the red-shift is mainly connected with the crystalline quality of the films.

In previous reports, ZnO thin films usually have two luminescent regions,[19,20] namely a sharp and strong ultraviolet emission peak and a wide and weak green emission band. For the ultraviolet emission, it is generally considered that it results from transition of electrons between the valence band and conduction band or/and a recombination of free exciton. However, visible emissions are connected with defects like oxygen vacancy, Zn interstitial and so on. As for the green emission, many researchers think it is related to oxygen vacancy.[21,22] There are many factors which affect the luminescence of ZnO thin films. Even if the ZnO thin films were prepared by the same technique, their luminescent properties may be different from one another. For example, while Hsieh,[23] Zhang,[24] Lan[25] *et al.* prepared ZnO thin films all by the sol–gel method on Si substrates, there is only ultraviolet emission in the films prepared by Hsieh *et al.* and there is only green emission in the films prepared by Lan *et al.* However, there are both ultraviolet emission and green emission in the films prepared by Zhang *et al.*

Regarding the ZnO thin films prepared by us, their photoluminescence properties are different. As shown in Fig. 4, sample A has a strong ultraviolet emission, but has almost no visible emission. Sample B has a reduced ultraviolet emission compared with sample A and a weak blue emission centered at 470 nm. For sample C, in contrast with sample B, its ultraviolet emission decreases but blue emission increases. As for the blue emission of ZnO thin films, it has been reported in many

papers.[26−28] For example, in Ref. 26, Wei *et al.* reported that they prepared ZnO thin films by pulsed laser deposition on sapphire substrates and found the films had a blue emission centered at about 462 nm. Wei *et al.* thought that the blue emission is connected with Zn interstitial and Zn vacancy. For the ZnO thin films prepared by the sol–gel method, they have a good stoichiometry of Zn and O. Therefore, there is no green emission related to oxygen vacancy in our films. But probably, there are some Zn interstitials and Zn vacancies in samples B and C, which led to the weak blue emission.

From the above analyses, it can be seen that substrate temperature also has an effect on the optical properties of ZnO thin films prepared by the sol–gel dip-coating method.

4. Conclusion

The sol–gel dip-coating method is an important method for fabrication of ZnO thin films. Therefore, it is meaningful to study how to optimize the preparation routine for improving the quality and preparation efficiency of ZnO thin films. In this work, we found that substrate temperature had an effect on crystalline quality and optical properties of ZnO thin films prepared by the sol–gel dip-coating process. If the substrate temperature is relatively high, the prepared ZnO thin film will have a poor crystalline quality and a weak ultraviolet emission. Therefore, the substrate and ZnO sol should have the same temperature when the sol–gel dip-coating method is used to prepare ZnO thin films. However, if the substrate which has just been given a pre-heat treatment must be cooled down to room temperature, only the next dip-coating can be carried out. It needs a period of time to eliminate heat, so that the film will have more chance to absorb the pollutants in air, which will affect the quality of the film. On the other hand, more time is needed to finish a desired film because the procedure from dip-coating to pre-heat treatment is repeated for several times to make the film reach a desired thickness. From the angle of improving the quality and preparation efficiency of ZnO thin films, we should take measures to quickly cool down the substrate after it has been given a drying and pre-heat treatment.

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