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Effect of aging time of ZnO sol on the structural and optical properties of ZnO thin films prepared by sol–gel method

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ABSTRACT

In this work, ZnO thin films were prepared by sol–gel method and the effect of aging time of ZnO sol on the structural and optical properties of the films was studied. The structural characteristics of the samples were analyzed by an atomic force microscope and an X-ray diffractometer. The optical properties were studied by a UV–vis spectrophotometer and a fluorophotometer. The results show that the ZnO thin film prepared by the as-synthesized ZnO sol had relatively poor crystalline quality, low optical transmittance in the visible range and relatively weak ultraviolet emission performance. After the as-synthesized ZnO sol was aged for 24 h, the degree of the preferred crystal orientation along the *c*-axis of the ZnO thin film prepared by this aged sol was improved. At the same time, this film had a very smooth surface with uniform grains and both its visible range transmittance and ultraviolet emission intensity were obviously increased. These results suggest that appropriate aging of ZnO sol is very important for the improvement of structural and optical quality of ZnO thin films derived from sol–gel method.

1. Introduction

ZnO is an important semiconductor material with excellent chemical and thermal stability at room temperature. At present, the preparation and application research of ZnO thin films attract many people' interest. At the early stage of the studies on ZnO materials, most interest was focused on the ultraviolet emission performance of ZnO thin films [1–3]. It is because ZnO has a direct wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. These characteristics make ZnO thin films have good excitonic emission performance. However, with the more learning about ZnO thin films, people come to realize that ZnO thin film is actually a multifunctional material. In addition to the application in ultraviolet emission devices [4,5], ZnO thin films also have important potential applications in non-volatile memory [6], PH sensors [7], varistors [8], surface acoustic wave devices [9], optical waveguides [10], solar cells [11], biosensors [12], etc. Therefore, many researchers in different fields are all interested in ZnO thin films.

So far, ZnO thin films have been prepared by many techniques such as molecular beam epitaxy, pulsed laser deposition, metal–organic chemical vapor deposition, magnetron sputtering, electron beam evaporation, spray pyrolysis, sol–gel method, etc. Compared with other techniques, sol–gel method has many advantages such as low cost, simple deposition equipment, easy fabrication of large-area films, easier adjustment of composition, being able to carry out doping at molecular level. Especially, it is suitable for the fabrication of multi-component metal oxide thin films. Owing to the above-mentioned advantages, sol–gel method has attracted much attention [13–16]. How to prepare high-quality ZnO thin films by sol–gel method has become a research subject. Although the sol–gel method is a relatively simple technique compared with other film deposition techniques, there are still many factors affecting the quality of ZnO thin films derived from the sol–gel method. The factors include ZnO sol concentration [17], sol chelating agent [15], pre-heating temperature [18], post-annealing temperature [16], sol aging temperature [19], withdrawing speed [20] and so on. Many results about effects of ZnO sol concentration and annealing treatment on ZnO thin films have been reported, but the effect of ZnO sol aging time on the quality of ZnO thin films is seldom studied. It is well known that the sol–gel method is a wet chemical technique; the properties of the sol have important effect

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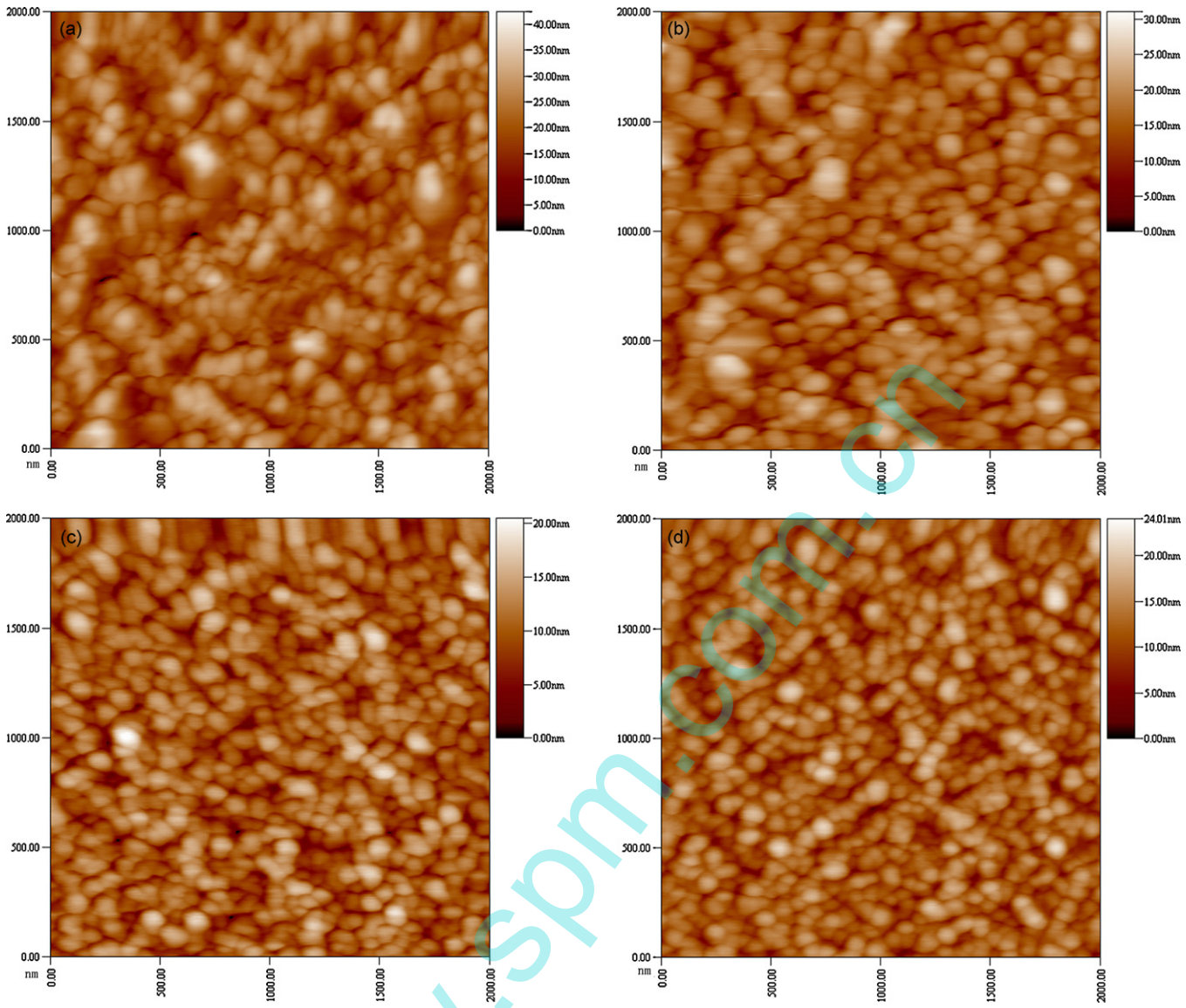

Fig. 1. Surface morphology images of samples A (a), B (b), C (c) and D (d).

on the physical properties of ZnO thin films. In the process of aging, some properties of the sol will change. Therefore, to study the effect of sol aging time on the quality of ZnO thin films is important.

Recently, some groups prepared ZnO thin films by spray pyrolysis and studied the effect of aging time of ZnO starting solutions on the films [21–23]. They found that the aging time had influence on the electrical and optical properties of ZnO thin films. For the sol–gel derived ZnO thin films, Fathollahi and Amini [24] once found that a threefold increase in the intensity of (0 0 2) reflection of ZnO films using a 3-week-aged zinc acetate solution in comparison to the freshly prepared solution when all the other variables were kept fixed. However, to our knowledge, Fathollahi and Amini did not carry out further studies on sol aging effect. The above-mentioned studies mainly focused on long-time (over 10 days) aging effect of the ZnO starting solutions. Considering the practical application, people always hope to prepare ZnO thin films using the sol as soon as possible. Therefore, to study the short-time aging effect of ZnO sol is more important. Furthermore, some research results have showed that the ZnO sols were still stable after aged for a month [25,26]. Thus, in this work, we studied the effect of short aging time (0–36 h) of ZnO sol on the structural and optical properties of ZnO thin films.

2. Experiments

ZnO sols were prepared using zinc acetate, anhydrous ethanol and monoethanolamine (MEA) as the solute, solvent and sol stabilizer, respectively. Zinc acetate was first dissolved in ethanol at room temperature, and then MEA was put into the solution. The molar ratio of MEA to zinc acetate was kept at 1.0. The resulting solution was stirred by a magnetic stirring apparatus at 70 °C for an hour. At last, a transparent ZnO sol was formed. In the sol, the Zn concentration was 0.25 mol/L. The same four ZnO sols were aged for 0, 8, 24 and 36 h, respectively. Then ZnO thin films were prepared by a spin-coating method on glass substrates which had been cleaned thoroughly and dried. The spin-coating time was 30 s. In the beginning 10 s, the spin-speed of the glass substrate was 1500 rpm; in the latter 20 s, the spin-speed was 3000 rpm. After each coating, the sample was first dried at 100 °C for 5 min, and then was pre-annealed at 320 °C in ambient atmosphere for 6 min. The procedures from spin-coating to pre-annealing were repeated for several times to make the film reach the desired thickness. At last, all the samples were post-annealed at 500 °C in ambient atmosphere for an hour. The films prepared by 0, 8, 24 and 36 h aged sols were labeled as samples A–D, respectively.

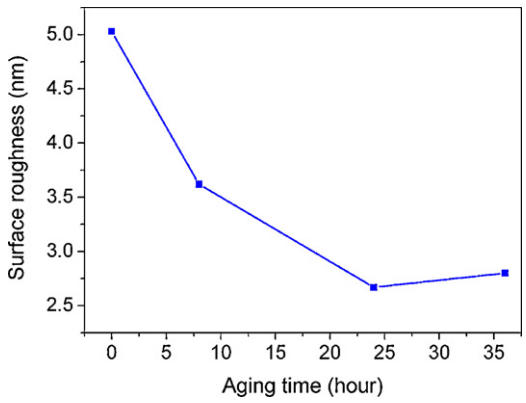

Fig. 2. The relationship graph of surface roughness and sol aging time.

The structural characteristics of the samples were analyzed by an atomic force microscope (CSPM4000) and an X-ray diffractometer (Bruker D8 Advance). The transmittance of the samples was measured by a UV–vis spectrophotometer (TU-1901). The photoluminescence spectra were used to study the luminescent behavior of the films. The light source was a Xe lamp and the excitation wavelength was 325 nm. All the measurements were carried out in air at room temperature.

3. Results and discussion

3.1. Effect of sol aging time on the structural properties of ZnO thin films

Fig. 1 shows the two-dimensional surface morphology images of ZnO thin films prepared by ZnO sols with different aging time. The images were obtained with an atomic force microscope by contact mode. The scanning area is 2 μm × 2 μm. Fig. 2 shows the root-mean-square surface roughness of the films. As for sample A, its surface is relatively rough and grain sizes are non-uniform. However, with the increase of sol aging time, the surface roughness gradually decreases and the ZnO grains get more and more uniform. For samples C and D, both of them have smooth surface and uniform grains. That is to say, the difference in surface features is very little. This means the sol had been very stable and homogenous after it was aged for 24 h. Therefore, ZnO thin films derived from sols aged over 24 h have good surface characteristics. For the as-synthesized sol, it is not stable enough. The sizes of ZnO colloidal-particles and the distribution of colloidal-particles are possibly non-uniform in the sol. As a result, the film derived from the as-synthesized sol has a relatively rough surface and non-uniform grains. With the increase of sol aging time, the sol gets more and more stable and homogenous. Accordingly, the quality of ZnO thin films prepared by aged sols is improved.

Fig. 3 displays the X-ray diffraction patterns of the samples. All the films show a diffraction peak at 34.4° or so, which corresponds to the reflection of the (0 0 2) plane of wurtzite-structured ZnO. This suggests that all the samples have a wurtzite structure and are preferentially oriented along the *c*-axis which is perpendicular to the substrate surface. It is clear from Fig. 3 that the intensity of (0 0 2) peak gradually increases with the prolonging of sol aging time. This result is similar to that reported by Fathollahi and Amini [24]. Fathollahi and Amini think that the sol aging can cause further condensation of the active groups and aggregation of zinc species in the solution and consequently may lead to the significant growth of the zinc oxide (0 0 2) reflection [24]. Both we and Fathollahi and Amini found that the sol aging can improve the degree of preferred crystal orientation along the *c*-axis, and it did not change the crystal growth orientation. However, when Guerra et al. [21] and Rozati et al. [23] prepared ZnO thin films by spray pyrolysis, they found the aging time of the starting solution had a great effect on the crystal growth orientation. For example, Guerra et al. [21] found the ZnO thin film deposited at 500 °C by 1-day aged solution was preferentially oriented along the (0 0 2) direction, but the ZnO thin films deposited by the starting solution with aging time more than 1 day were preferentially oriented along the (1 0 0) direction in turn. In spite of the deposition technique difference, all the above-mentioned results show that the aging time of the starting solution have influence on the structures of ZnO thin films. As for the sol–gel method, our results suggest 24 h aged ZnO sol is ideal for fabrication of high-quality ZnO thin films.

3.2. Effect of sol aging time on the optical properties of ZnO thin films

Fig. 4 shows the transmittance spectra of the samples. All the samples have a transmittance over 65% in the visible range. Especially for samples C and D, both their average transmittance in the visible range is above 90%. With the increase of sol aging time, the transmittance of ZnO thin film in the visible range is gradually improved. However, sol aging time does not affect the strong absorption property of ZnO thin films in the ultraviolet range and the absorption edges of the samples all lie at ~370 nm. In here, there are two major factors affecting the transmittance, namely, surface scattering and grain-boundary scattering. From Figs. 1 and 2, it can be known that the surface of sample A is relatively rough and its grain-boundary is irregular, so the surface scattering and grain-boundary scattering of sample A are strong, accordingly inducing

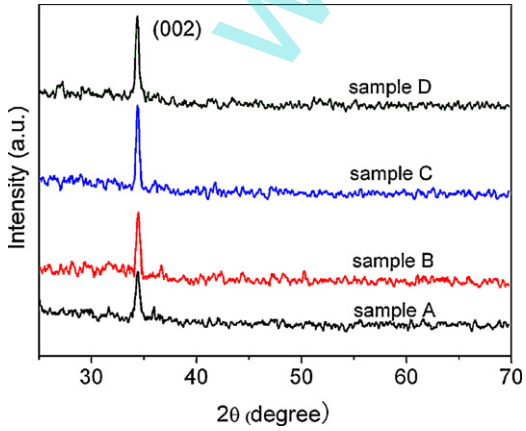

Fig. 3. X-ray diffraction patterns of the samples.

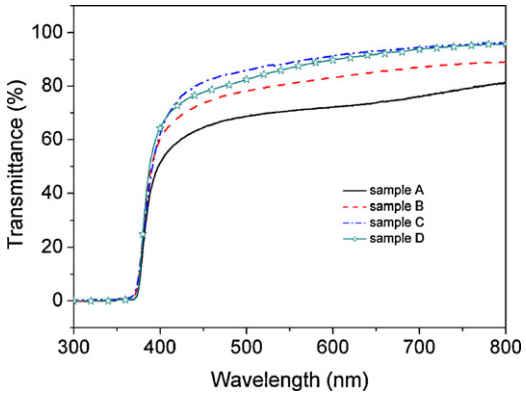

Fig. 4. Transmittance spectra of the samples.

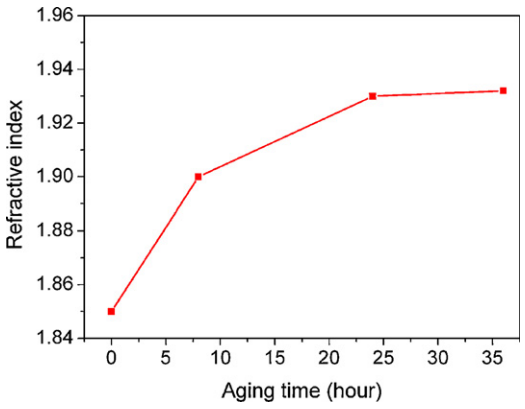

Fig. 5. The relationship graph of refraction index and sol aging time.

a low transmittance in the visible range. As for other samples, on the one hand, surface roughness is decreased; on the other hand, the grain sizes are more uniform and grain-boundary is clear and regular. As a result, the transmittance of samples B–D is increased.

Refraction index is an important parameter reflecting the optical quality of ZnO thin films. At the same time, it can also reflect the degree of crystalline quality of ZnO thin films [27]. Fig. 5 gives the refraction indexes of the samples measured by an ellipsometer with a He–Ne laser as light source ($\lambda = 632.8$ nm). When the samples were measured, three measurement spots were picked on each sample at random. The average of the three measured values was used as the refraction index of the sample. It is clear from Fig. 5 that with the increase of sol aging time (up to 24 h), the refraction index gradually increased, which meant the crystalline quality of ZnO thin films was improved [27]. However, when the sol aging time was prolonged from 24 to 36 h, the refraction index hardly changed which seemed to come to saturation. This phenomenon is similar to the change of the transmittance and the (0 0 2) peak intensity of the samples. It shows that sol aging time has little effect on the structural and optical properties of ZnO thin films when ZnO sol is aged from 24 to 36 h.

Fig. 6 shows the room temperature photoluminescence spectra. The samples all have an ultraviolet emission peak centered at 383 nm. For samples A and B, besides the ultraviolet emission peak, they also have a weak blue emission peak located at 470 nm. With the prolonging of sol aging time, the intensity of ultraviolet emission is increased and the full width of half maximum of the emission peak is decreased. With respect to the room temperature ultraviolet emission of ZnO, it is widely accepted that the ultraviolet emission results from the recombination of free exciton [2,13].

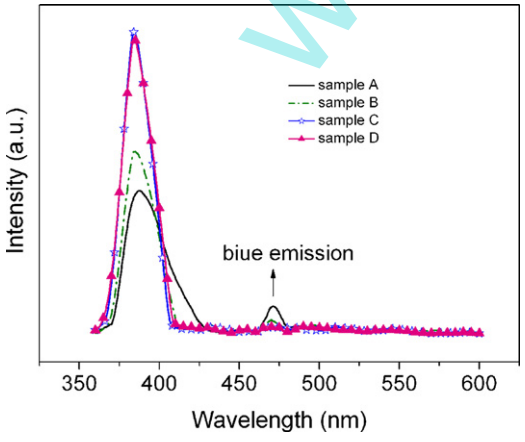

Fig. 6. Photoluminescence spectra of the samples.

Therefore, the density of free exciton in ZnO decides the ultraviolet emission performance to a large extent. From Fig. 6, it can be seen that the ultraviolet emission is gradually increased with the prolonging of sol aging time. It is mainly because the density of free exciton is increased due to the improvement of crystalline quality of ZnO thin films. Dong et al. [28] also found the ultraviolet emission performance of ZnO nanocrystalline powder prepared by aged ZnO sol was improved compared with that of ZnO nanocrystalline powder prepared by as-synthesized ZnO sol. They think that it is a result of improvement of crystal quality of ZnO powder.

For the blue emission of ZnO materials, some experimental results have been reported [29–32]. So far, the blue emission mechanism is still unclear. For example, Wang et al. [29] investigated the effect of oxygen pressure on photoluminescence of ZnO thin films prepared by RF magnetron sputtering. They found that the deposited films had a blue emission peak centered at 468 nm and they attributed the blue emission to the electron transition between the oxygen vacancies and interstitial oxygen. Ning and Li [30] studied the effect of annealing treatment on photoluminescence of ZnO thin films prepared by RF magnetron sputtering. They found that the films also had a blue emission peak around 470 nm. The blue emission gradually increased with the increasing annealing temperature from 150 to 650 °C, but reduced when annealing temperature increased from 650 to 850 °C. Ning and Li think the blue emission is connected with Zn vacancies [30]. Ghosh and Choudhary [31] prepared ZnO thin films by a cost-effective vacuum-carbon-arc technique combined with thermal oxidation under ambient conditions from zinc nanoparticles in carbon matrix. They found that these films had not only blue emission (~486 nm) but also violet emission (~423 nm) and green emission (~521 nm). By analyzing the possible point-defect density in the films, Ghosh et al. think the blue emission is mainly associated with Zn vacancy and Zn interstitial. We tend to support the view of Ghosh and Choudhary. On the one hand, sol–gel method offers a rich-oxygen growth environment for ZnO thin films; on the other hand, we annealed the films at a medium temperature (500 °C). That is to say, both the growth and annealing environment will not induce many oxygen vacancies. Therefore, the density of oxygen vacancy in our samples should be low. However, there are possibly some Zn vacancies and Zn interstitials in the films, which lead to the weak blue emission. With the prolonging of sol aging time, the crystalline quality of ZnO thin films is improved; accordingly, the blue emission is also decreased.

4. Conclusions

ZnO thin films were prepared by sol–gel method and the effect of sol aging time on the structural and optical properties were investigated. The results show that ZnO thin films deposited by as-synthesized sol have relatively rough surface, non-uniform grains, low visible range transmittance and weak ultraviolet emission performance. It is possibly because the as-synthesized sol is not stable enough in which the colloidal-particle sizes and colloidal-particle distribution are non-uniform. As a result, the film deposited by the as-synthesized sol has relatively poor quality. With the prolonging of sol aging time, the structural and optical properties of ZnO thin films are improved gradually. The ideal aging time is suggested 24 h. On the one hand, the film prepared by 24 h aged sol has good quality; on the other hand, 24 h is not too long and it will not affect the film preparation efficiency.

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