



Structural and optical properties of ZnO thin films prepared by sol–gel method with different thickness

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ABSTRACT

In this work, ZnO thin films with different thickness were prepared by sol–gel method on glass substrates and the structural and optical properties of these films were studied by X-ray diffractometer, atomic force microscope, UV–visible spectrophotometer, ellipsometer and fluorophotometer, respectively. The structural analyses show that all the samples have a wurtzite structure and are preferentially oriented along the *c*-axis perpendicular to the substrate surface. The growth process of highly *c*-axis oriented ZnO thin films derived from sol–gel method is a self-template process. With the increase of film thickness, the structural disorder decreases and the crystalline quality of the films is gradually improved. A transition of crystal growth mode from vertical growth to lateral growth is observed and the transition point is found between 270 and 360 nm thickness. The optical analyses show that with the increase of film thickness, both the refractive index and ultraviolet emission intensity are improved. However, the transmittance in the visible range is hardly influenced by the film thickness, and the averages are all above 80%.

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1. Introduction

As a new-generation multifunctional semiconductor material, ZnO thin film has received extensive attention in recent years. Due to the direct wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO thin films are considered as the ideal materials for the fabrication of short-wavelength optoelectronic devices such as ultraviolet lasers [1], ultraviolet light-emitting diodes [2], ultraviolet photoconductive detectors [3]. ZnO thin films usually have high transmittance in the visible range and possess excellent n-type conductivity when doped with Al, Ga and In, so they can be used as transparent electrodes [4] and window layers [5] in solar cells. Furthermore, ZnO thin films also have potential applications in thin film transistors [6], optical waveguides [7], gas sensors [8], diluted magnetic semiconductor devices [9], and surface acoustic wave devices [10] and so on.

So far, ZnO thin films have been prepared by many techniques such as molecular beam epitaxy, atomic layer epitaxy, metal-

organic chemical vapor deposition, spray pyrolysis, sol–gel method, pulsed laser deposition, magnetron sputtering, electron beam evaporation. Among these techniques, sol–gel method attracts much attention due to some distinct advantages including low cost, simple deposition equipment, easier adjustment of composition, being able to carry out doping at molecular level, easy fabrication of large-area films and so on. Many research groups have prepared ZnO thin films by sol–gel method and used them to fabricate optoelectronic devices. For example, Ma et al. used the sol–gel derived ZnO thin films to fabricate ultraviolet random laser [11]; Park et al. utilized the sol–gel derived ZnO thin films to fabricate thin film transistor [11]; Kyaw et al. applied the sol–gel derived ZnO thin films to organic solar cell [12]. Although the sol–gel method is a relatively simple technique for preparing ZnO thin films, there are still many factors affecting the physical properties of ZnO thin films. These factors include ZnO sol concentration [13], preheating temperature [14], post-annealing temperature [15], annealing atmosphere [16], film thickness [17] and so on. Among these factors, the influence of film thickness on structural, optical and electrical properties of ZnO thin films (especially undoped ZnO thin films) derived from sol–gel method was less studied. Even for the previously reported results, there are still many differences between them. For example, Sharma and Mehra [17] prepared

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highly *c*-axis oriented ZnO thin films by sol–gel method; they found a transition of growth mode from vertical growth to lateral growth of the ZnO thin film with the increase of thickness. Mridha and Basak [18] also prepared ZnO thin films with different thicknesses by sol–gel method. However, these films were basically randomly oriented except that one with 260 nm thickness which was preferentially oriented along the *c*-axis direction. No transition of growth mode was observed, but Mridha et al. found that the ZnO thin film with 260 nm thickness had the best crystallization, optical and electrical properties. In order to obtain high-quality optoelectronic devices based on ZnO thin films, it is very important to deeply investigate the influence of the film parameters such as film thickness on the microstructure and optical properties. In this work, ZnO thin films with different thickness were prepared by the optimized sol–gel technique on glass substrates and the structural and optical properties were deeply studied. Based on the analyses of X-ray diffraction (XRD) and atomic force microscope (AFM), a growth mechanism of highly *c*-axis oriented ZnO thin films derived from sol–gel method was proposed.

2. Experiments

The ZnO sol was prepared using zinc acetate, anhydrous ethanol and monoethanolamine (MEA) as the solute, solvent and sol stabilizer, respectively. Zinc acetate was first dissolved in ethanol, and then the resulting solution was stirred by a magnetic stirring apparatus in hot water bath at 70 °C. At the same time, MEA was put into the solution drop by drop. The molar ratio of MEA to zinc acetate was kept at 1.0. After 2 h, a transparent ZnO sol was formed. In the sol, the Zn concentration was 0.35 mol/L. After the ZnO sol was aged for 24 h at room temperature, ZnO thin films were prepared by dip-coating this ZnO sol on glass substrates which had been thoroughly cleaned and dried. After each coating, the sample was first placed under an infrared lamp to be dried for 8 min, and then was put into a furnace at 350 °C for preheating treatment for 6 min. The above-mentioned procedures from dip-coating to a preheating treatment were repeated for 3, 6, 9 and 12 times in order to get the films with different thicknesses; correspondingly, the films were labeled as samples A, B, C and D, respectively. All the samples were post-annealed at 500 °C in air for 1 h. The average thickness of each single layer measured by an ellipsometer was ~30 nm. Therefore, the thickness of samples A, B, C and D was about 90, 180, 270 and 360 nm, respectively.

The crystal phase and crystalline orientation of the ZnO thin films were analyzed by an X-ray diffractometer with a Bragg–Brentano geometry (Bruker D8 Advance). The surface morphology was observed by an atomic force microscope (CSPM4000) in contact mode. The film thickness and refractive index were measured by an ellipsometer (TPY-2). The transmittance was recorded by a UV–visible spectrophotometer (TU-1901). The photoluminescence spectra were used to study the luminescent property of the films. The light source was a Xe lamp and the excitation wavelength was 325 nm. All the measurements were performed in air at room temperature.

3. Results and discussion

3.1. The dependence of structural property of ZnO thin film on thickness

Fig. 1 shows XRD patterns of ZnO thin films with different thickness. All the diffraction peaks in the patterns correspond to the reflection of wurtzite-structured ZnO planes and all the samples have a strong (002) peak. This suggests that all the prepared ZnO thin films have a hexagonal wurtzite structure and are prefer-

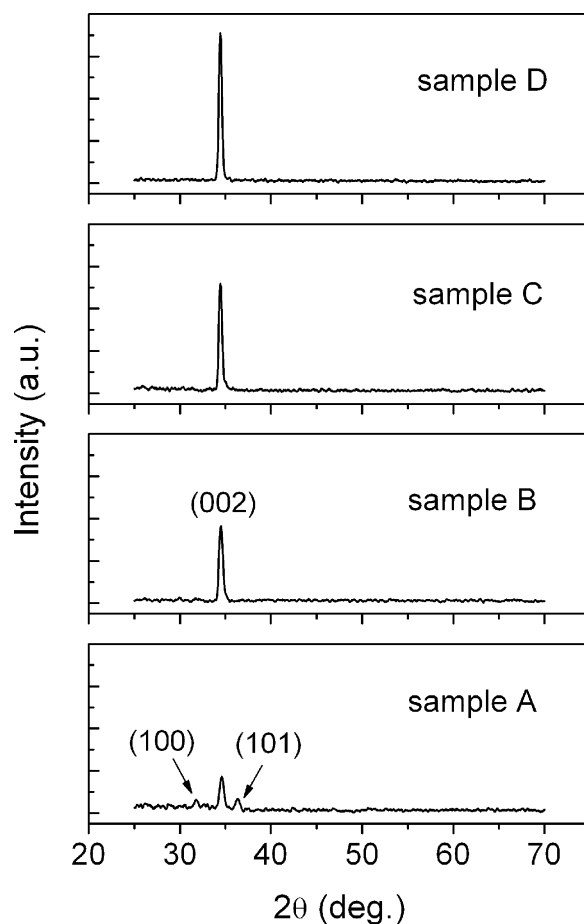


Fig. 1. XRD patterns of ZnO thin films with different thickness.

entially oriented along the *c*-axis perpendicular to the substrate surface. As for sample A, besides the (002) peak, it still has two other peaks, namely (100) peak and (101) peak. With the increase of film thickness, the intensity of (002) peak is increased, but the full width at half maximum (FWHM) is decreased as shown in Fig. 2. The similar results were also reported by others [19,20]. It means that within a certain range of thickness, the crystalline quality of ZnO thin films is gradually improved with the increase of film thickness. The positions of the (002) peaks are shown in Fig. 2. The strain along the *c*-axis for the samples was calculated by the following formula:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\% \quad (1)$$

where *c* is the lattice parameter of the sample calculated from XRD data and *c*₀ is lattice parameter of ZnO crystal without strain. From Fig. 2, it can be seen that the strain gradually decreases with the increase of film thickness. This is similar to the result reported by Dong et al. [19]. However, Mridha and Basak [18] found that the strain along the *c*-axis is decreased as the film is grown up to a thickness of 300 nm. Above 300 nm, the strain again becomes appreciable. We think the difference of strain in ZnO thin films prepared by us and Mridha et al. is mainly connected with the preparation conditions and thermal treatment. For example, in the film preparation process, we adopted three-step thermal treatment, namely infrared drying, pre-heating at 350 °C, and post-annealing at 500 °C for 1 h, but Mridha and Basak [18] adopted two-step thermal treatment, namely drying at 120 °C and annealing at 550 °C for 30 min. In fact, a 30-min annealing time is not long enough to eliminate the strain in the film. Therefore, from

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