Characteristics of Quartz-based ZnO Films Grown by Pulsed Laser Deposition

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Abstract: ZnO thin films were grown on quartz at various substrate temperatures by pulsed laser deposition (PLD). X-ray diffraction (XRD) and UV–VIS spectrophotometry were used to analyze various structural and optical parameters. The effect of substrate temperature on crystal quality and optical properties of quartz - based ZnO films was studied. XRD showed that an optimal crystallized ZnO thin film was observed at the substrate temperature of 500℃. Transmission spectrum and its differential spectrum obtained by spectrophotometer indicates that the bandgap width of ZnO film decreases with the increase of substrate temperature.

Keywords: *PLD, ZnO, XRD, Quantum Constraint effect, Bandgap*

I. INTRODUCTION

Zinc oxide (ZnO) as a transparent conductive oxide (TCOs) has important applications in scientific research and production. It has a wide direct bandgap (3.37 eV) and belongs to the group II-VI composite semiconductor, whose exciton binding energy can be as high as 60meV. Due to the presence of interstitial zinc and vacancy oxygen, undoped ZnO is N-type in nature. An external dopant is required to improve the conductivity of the material. Both doped and undoped ZnO films crystallize in wurtzite structure. The advantages of ZnO include low cost, abundant resources, non-toxic, suitable for mass production, and easier availability compared to other TCOs. There are many methods for preparing zinc oxide films, such as magnetron sputtering method [1], spray pyrolysis method [2], sol-gel method [3], pulse laser deposition (PLD) method [4] and so on. Among them, the advantages of PLD method are: the substrate temperature requirements are low, the preparation of the film is relatively uniform, the composition will not change, the process parameters can be arbitrarily adjustable, the synthesis process allows relatively high oxygen content. Therefore, PLD method is an effective method to synthesize oxide semiconductor materials, which is paid more and more attention.

Most studies on ZnO thin films are based on silicon or sapphire substrates. In recent years, in order to meet the needs of preparing new functional thin film materials, many kinds of substrates and new processes have been tried. In this paper, we use PLD technology to prepare crystalline ZnO thin films with quartz as substrate at various substrate temperatures, and quantitatively analyze the properties of the prepared ZnO thin films with a variety of parameters.

II. EXPERIMENT

The ZnO thin films were prepared by pulsed laser deposition (PLD). The Nd: YAG pulsed laser was used. The wavelength of the laser was 1064 nm, the energy of each laser pulse was 200 mJ, the spot area of the laser beam was 0.43 mm2, the energy density of 47 J· cm-2 was generated, the repetition rate was 10 Hz, and the pulse width was 10 ns.

The target material is high purity ZnO (99.9%) solid prepared by sintering, and the substrate is amorphous quartz cleaned by ultrasonic and distilled water. The substrate was placed parallel to the target surface at a distance of 4 cm, and the system was vacuumed to 2.0×10-4 Pa. The substrate temperature was heated to 200℃, 300 ℃, 400 ℃, 500 ℃ and 600 ℃, and then 100mPa high purity oxygen (99.999%) was filled. The focused pulsed laser beam entered the vacuum cavity through the optical window, and the ZnO target was ablated at a direction of 45° with the target surface. After irradiation, the target absorbs high density energy and forms a plasma state, which is deposited on the substrate on the opposite side to form a film. The deposition time was 15 min, and the sample was taken out after it was reduced to room temperature.

Subsequently, the structure and optical properties of the films at all substrate temperatures were characterized. The Rigaku Miniflex X-ray diffractometer (Cu target Kα ray, wavelength: 0.154178 nm) was used to analyze the structural characteristics of the deposited films with 2θ ranging from 20° to 80°. The step size was 0.02. The transmittance of ZnO films was measured by SHIMADZU UV/VIS/NIR 1800 spectrophotometry in the wavelength range of 300~1100 nm.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

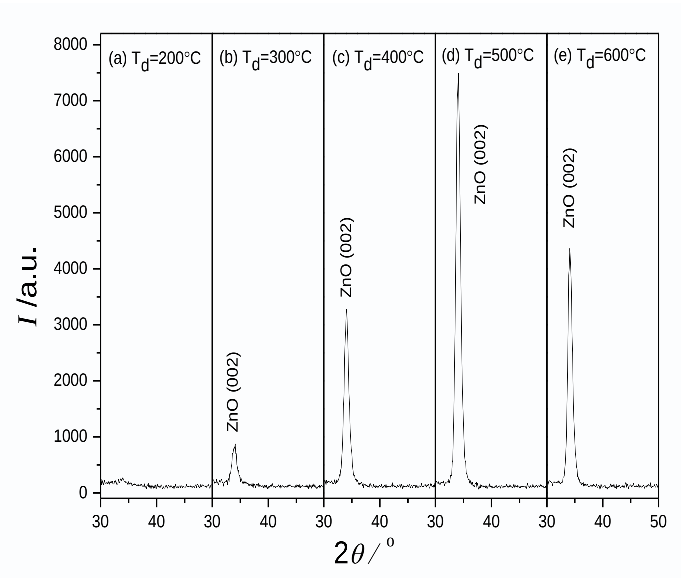

Fig.1 XRD spectra obtained from ZnO films deposited at substrate temperatures of (a) 200, (b) 300, (c) 400, (d) 500, (e) 600 ℃

Figure 1 shows the XRD patterns of 2θ in the range of 30°~50°.

It can be seen that there is a steep diffraction peak near 2θ = 34°, which is consistent with the standard card of the ZnO (002) plane, so the corresponding crystal plane is the ZnO (002) plane. These films are polycrystalline in nature and have a C-axis perpendicular to the substrate surface as the preferred growth direction, with a highly consistent final orientation. When the substrate temperature is low, the energy of O atoms and Zn atoms adsorbed on the quartz surface is low, and the atoms are deposited nearby. Therefore, the crystallinity of ZnO is poor. With the increase of substrate temperature, the O and Zn atoms on the quartz surface gain enough energy to grow in the preferred C-axis orientation, and the crystal quality of the film is improved. When the substrate temperature is too high, the adsorption atoms have a large kinetic energy, but at the same time, the desorption on the substrate surface is intensified, which leads to the decrease of crystallization quality. The grain size can be calculated using the Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

Where, D is the grain size, λ is the wavelength of X-ray, θ is the diffraction Angle, β is the half-height width of the diffraction peak of XRD (002). The grain size increases with the decrease of the half-height width of the diffraction peak.

Since ZnO belongs to the hexagonal crystal system, for the hexagonal crystal system, the crystal plane spacing is determined by the following formula:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \qquad (2)$$

Where, d is the crystal plane spacing, a, b and c are the fundamental vectors of the hexagonal lattice, namely, lattice constants. h, k and l are crystal plane indices. For ZnO (002) diffraction peak, h=k=0, l=2, according to equation (2), c=2d. From Bragg's formula:

$$2d\sin\theta = n\lambda \qquad (3)$$

According to Equation (3), we can calculate the crystal plane spacing d of ZnO(002) and the lattice constant 2d of C-axis.

Table 1 lists the variation of various parameters of ZnO films measured in the experiment and calculated based on the measurement results as a function of substrate temperature. As can be seen from Table 1, with the increase of substrate temperature, the half-height width of the diffraction peak of ZnO(002) generally decreases and the grain size increases. When the substrate temperature increases, the violent surface reaction favors the fluidity of the material [5] and leads to an increase in the grain size. However, the quality of crystallization is not only related to the grain size, but also related to the crystallinity. The higher the crystallinity, the greater the intensity of the diffraction peak. As shown in Table 1, when the substrate temperature is 500℃, the grain size has little difference compared with that at 600℃, while the XRD diffraction peak intensity of ZnO(002) is much larger, indicating that the substrate temperature has the highest crystallinity and the best crystal quality.

The value of strain (ε) along the C-axis is calculated using equation (4).

$$\varepsilon = \frac{d - d_0}{d_0} \times 100\% \quad (4)$$

Where, d is the crystal plane spacing of ZnO(002) calculated by Bragg equation (3), and d0 is the crystal plane spacing of powdered ZnO(002) without strain. The residual stress (σ) is calculated by using equation (5) through biaxial strain model [6].

$$\sigma = \frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{2C_{13}} \cdot \frac{d - d_0}{d_0} \qquad (5)$$

Where, the value of Cij (elastic constant of single crystal ZnO) is C11= 208.8GPa, C33 = 213.8GPa, C12= 119.7GPa, C13 = 104.2GPa, so the stress σ = -233εGPa.

It can be seen from Table 1 that the crystal plane spacing of ZnO films prepared at various substrate temperatures is larger than that of ZnO powders 0.2602 nm. Therefore, the strain and stress values of ZnO films at various substrate temperatures are calculated, as shown in Table 1. King[7] et al. believe that the generation of stress is related to lattice defects, thermal expansion coefficient mismatch and other factors. Among them, the internal stress is related to the lattice defects of the film, for example, zinc interstitial will produce compressive stress, and oxygen vacancy will produce tensile stress. However, the mismatch of thermal expansion coefficient is an external factor. For example, the thermal expansion coefficient of ZnO is 2.6×10-6 K-1, which is larger than that of quartz 0.51×10-6 K-1 [8]. The ZnO films grown at the substrate temperature of 200℃~600℃ all show compressive stress, and the value of compressive stress decreases gradually with the increase of substrate temperature. This means that the higher substrate temperature provides sufficient thermal energy for the film, so that part of the stress is released at high temperature.

Tab.1 Characteristic parameters of ZnO(002) grown at different substrate temperatures

衬底温度/℃	XRD 2θ/°	XRD衍射峰半高宽/°	晶粒尺寸/nm	XRD衍射峰强度/a.u.	晶面间距/nm	应变/%	应力/GPa	禁带宽度/eV
200	33.82	1.4	5.87	257	2.6482	1.7365	-4.046	
300	33.96	1.32	6.23	831	2.6376	1.3292	-3.097	
400	34.06	1.14	7.21	3226	2.6301	1.0411	-2.426	3.31
500	34.08	1.12	7.34	7412	2.6286	0.9835	-2.292	3.26
600	34.12	1.08	7.61	4288	2.6256	0.8682	-2.023	3.21

B. Optical Characteristics

The transmission spectra of ZnO thin films in the wavelength range of 350~450 nm obtained by UV and NIR spectrometers are shown in FIG. 2. Because the crystallization quality is obviously poor when the substrate temperature is 200℃ and 300℃, we only characterized the zno films grown at 400℃,500℃ and 600℃. The average transmittance (T) of all zno films grown at three substrate temperatures is about 90%, and the transmittance of the films at 600℃ decreases slightly. This may be because when the substrate temperature is 600℃, the grain size increases, the surface roughness increases, and therefore the optical scattering increases [9]. The absorption edges of all films are in the wavelength (λ) range of 365 to 385 nm, which means that the band gap corresponds to the photon energy in this range of wavelength.

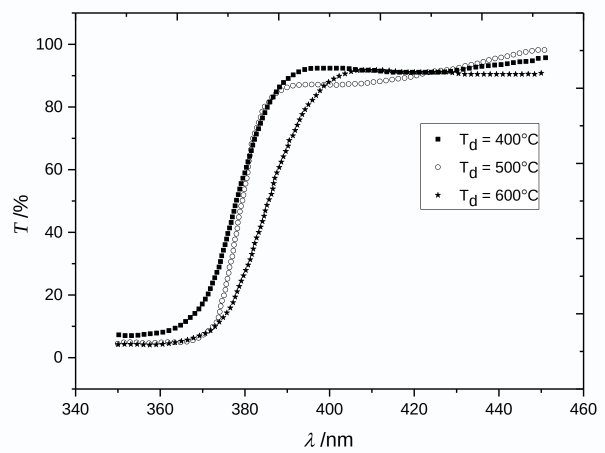

Fig.2 Transmittance graph of ZnO thin films grown at substrate temperatures of 400, 500 and 600℃

The gap width of the film can be calculated using equation (6) :

$$Eg = \frac{hc}{\lambda_{max}} \quad (6)$$

Where: h=4.13567×10-15 eV·s, c=3×1017 nm/s, λmax is the wavelength corresponding to the maximum value of the first derivative of transmittance (dT/dλ).

The transmittance map (Figure 2) was differentiated by software to obtain the curve of dT/dλ as a function of wavelength, as shown in Figure 3. The wavelength λmax corresponding to the maximum value of the curve is read out, and the band gaps of ZnO films grown at three substrate temperatures are calculated by Eq. (6). As shown in Table 1, the band gap decreases as the substrate temperature increases.

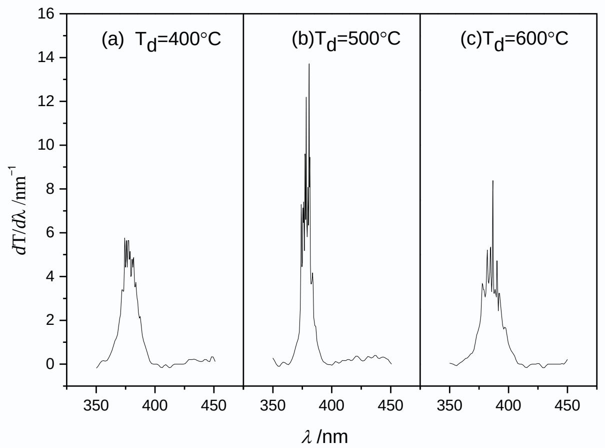

Fig.3 Curves of variation of dT/dλ with wavelength of ZnO thin films grown at substrate temperatures of 400, 500 and 600℃

It can also be seen from the transmission diagram that with the increase of substrate temperature, the absorption edge produces a red shift, thereby reducing the band gap [10]. This conclusion is correlated with XRD results. An increase in grain size (D) with increasing substrate temperature leads to a decrease in band gap, which is consistent with the results of quantum confinement effects. When the grain size (D) is equivalent to the exciton Bohr radius, the quantum confinement effect becomes very obvious. As the size of the quantum dot approaches the exciton Bohr radius, the movement of electrons in the solid is restricted, and the width of the semiconductor band gap also increases with the decrease of the material size.

CONCLUSION

Zinc oxide film was grown on quartz substrate by PLD method. The effect of substrate temperature on the structure and optical properties of the deposited films was studied quantitatively. The XRD results show that the grain size increases with the increase of substrate temperature, while the grain plane spacing, strain and stress decrease correspondingly. The crystallization quality of ZnO films is the best when the substrate temperature is 500℃. The transmission pattern shows that the grain size increases with the increase of substrate temperature, which is consistent with the XRD results. The differential pattern of the transmission pattern shows that the bandgap energy (Eg) decreases with the increase of substrate temperature, and the absorption edge moves to the red zone.

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