Zn/O ratio and oxygen chemical state of nanocrystalline ZnO films grown at different temperatures*

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ZnO nanocrystalline films are prepared on Si substrates at different temperatures by using metal-organic chemical vapour deposition (MOCVD). It is observed that when the growth temperature is low, the stoichiometric ratio between Zn and O atoms has a large deviation from the ideal ratio of 1:1. The ZnO grains in the film have small sizes and are not well crystallized, resulting in a poor photoluminescence (PL) property. When the temperature is increased to an appropriate value, the Zn/O ratio becomes optimized, and most of Zn and O atoms are combined into Zn–O bonds. Then the film has good crystal quality and good PL property. If the temperature is fairly high, the interfacial mutual diffusion of atoms between the substrate and the epitaxial film appears, and the desorption process of the oxygen atoms is enhanced. However, it has no effect on the film property. The film still has the best crystal quality and PL property.

Keywords: ZnO film, metal-organic chemical vapour deposition, growth temperature, Zn/O ratio

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1. Introduction

Recently, ZnO material has attracted much attention and been widely investigated due to its direct wide bandgap (3.3 eV at room temperature (RT)) and large exciton binding energy (60 meV).[1] The current key issue is how to realize p-type ZnO for commercial optoelectronic applications. So far, p-type ZnO can be acquired by monodoping of I or V group elements, such as N, P, Li, and K,[2−5] and by codoping of III, V group elements, such as Al, N.[6,7] However, repeatability and stability are still problems. One of the possible reasons causing the p-type doping difficulty is the high density of intrinsic low-energy defects, such as Zn interstitials (Zn_i) or O vacancies (V_O), which can compensate the p-type dopants.[1] In addition, these defects may act as energy levels and give rise to the yellow emission, which deteriorates the photoluminescence (PL) property. So it is very important to obtain ZnO films with good stoichiometry, high crystalline quality, and low residual impurity concentrations.[8] Besides the substrate effect,[9] it has been reported that the temperature plays a critical role during ZnO growth and can affect the growth mode, crystal quality, film stress and optical property.[10−12] Here, to obtain ZnO film with good stoichiometry and excellent properties, we investigate the influence of temperature on THE Zn/O ratio of the ZnO film and then examine its structural and optical properties.

2. Experiment

ZnO films can be grown by various deposition techniques, such as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), magnetron sputtering, filtered cathodic vacuum arc, and metal-organic chemical vapour deposition (MOCVD). Among them, MOCVD provides the advantage of growing high-quality films due to its versatility in controlling the various thermodynamic interactions. It also offers high growth rate, good growth efficiency, large area uniformity, and different doping processes. In this

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work, approximately 300 nm thick ZnO films are prepared at different temperatures by using a vertical low-pressure MOCVD system. The growth temperatures are set at 400 °C, 600 °C, 650 °C, and the three samples are denoted as samples A, B, C, respectively. Bubbled diethylzinc (DEZn) and pure oxygen are the reactants, and nitrogen gas is used as the carrier gas. The flow rates of the nitrogen-carrying DEZn and the pure oxygen gas are set at 49 standard cubic centimeters per minute (sccm) and 1 standard liter per minute (slm), respectively. The pressure of the chamber is kept at about 1.01×10^4 Pa.

The surface morphologies are measured by FEI Sirion-200 field emission scanning electron microscopy (FE-SEM). The crystal quality of the ZnO is measured by X-ray diffraction (XRD) on Philips X'Pert X-ray diffraction apparatus using Cu $K\alpha$ radiation. The Zn/O ratio of the film is detected by Rutherford back scattering (RBS). The X-ray photoelectron spectroscopy (XPS) performed with a PHI Quantera SXM spectrometer with monochromatic Al $K\alpha$ radiation source is used to analyse the chemical state of the oxygen. PL measurements are performed using an He–Cd laser (325 nm) as the excitation source at room temperature.

3. Results and discussion

Figure 1 shows the images of the surface and the cross-sectional FE-SEM of samples A, B, and C, from which we can easily find that their morphologies are very different, especially the morphology of sample A. When the growth temperature is low, the surface of the ZnO film is found to be continuous and dense, which illustrates that ZnO is in a two-dimensional (2D) growth mode. From the image of the cross section, we can find that ZnO nanocrystalline grains are small and look like flakes. When the temperature increases, the growth mode becomes three-dimensional (3D), and we can find that the film presents a column structure and the surface looks lumpy, as shown in the morphologies of samples B and C. These phenomena are also observed in Al-doped ZnO films on glass substrates prepared by radio-frequency (RF) magnetron sputtering.[13]

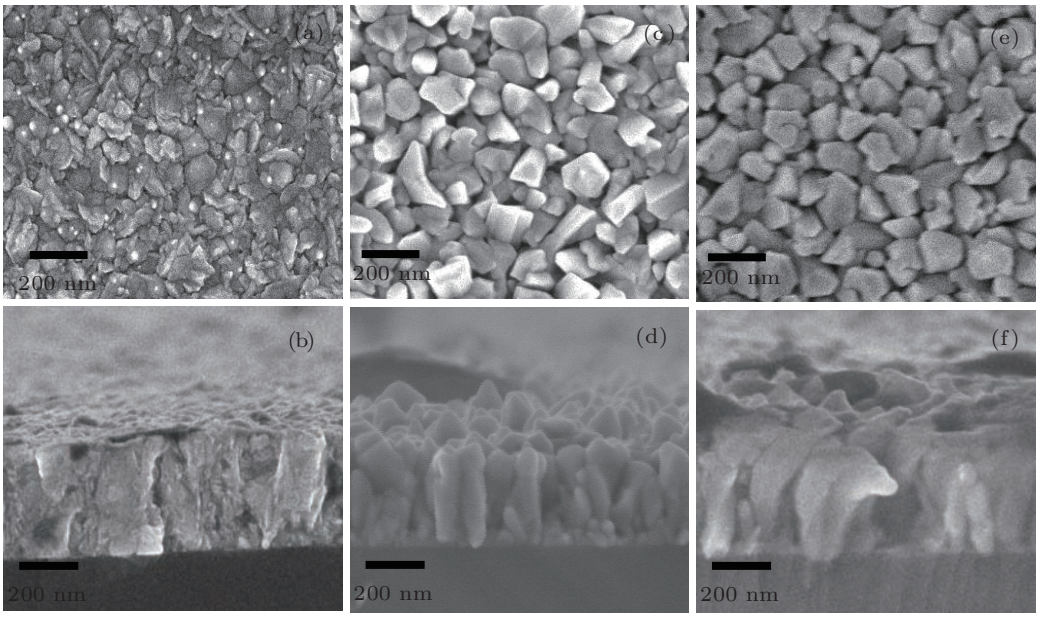


Fig. 1. SEM images of surfaces and cross sections of ZnO films grown at 400 °C ((a) and (b)), 600 °C ((c) and (d)), and 650 °C ((e) and (f)).

Table 1. XRD, RBS, and PL spectrum data of samples A, B, and C.

Sample	2θ/(°)	FWHM/(°)	Grain size/nm	Thickness/nm	Zn/O	UVL/DVL
A	34.582	0.454	19.1	345	0.57/0.43	1.25
B	34.475	0.206	42.1	235	0.53/0.47	2.89
C	34.433	0.149	58.3	350	0.56/0.44	8.20

The crystal qualities of the films are detected by XRD, and the spectra are shown in Fig. 2. It is observed that there are very significant peaks around 34.4° in the three samples, indicating that all samples are of high crystal quality and are of the wurtzite structure with an intense *c* orientation. The appearance of two weak peaks corresponding to ZnO (101) and (102) faces in sample A shows that there is a little portion of polycrystal in sample A. The details of the (002) peaks for the three samples, i.e., the accurate positions, the full widths at half maximum (FWHMs), and the calculated grain sizes, are summarized in Table 1. With the increase of the growth temperature, the FWHM of the (002) peak decreases dramatically, and the grain size increases correspondingly. These results are well consistent with the conclusion obtained from the SEM detection.

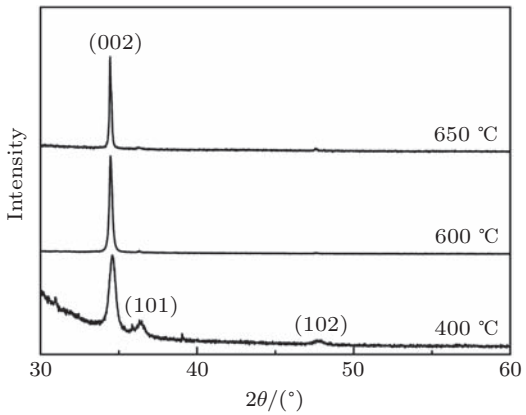


Fig. 2. XRD spectra of ZnO films grown at different temperatures.

The RBS test is an effective method to analyse the chemical compositions of thin films and the interface information between different compounds.[14,15] Figure 3 shows the RBS spectra, from which we can easily find the step signals of Zn, O, and Si. By using SIMNRA software, the data of the respective film thickness and the Zn/O ratio are obtained and summarized in Table 1. With the three growth temperatures, none of the samples are well stoichiometric, and all samples are slightly oxygen deficient. If the temperature is too low or too high, the situation tends to be worse. Our results are very different from and better than the reported ZnO films prepared by using the sputtering method in Ref. [16]. We believe this is because the preferential difference between Zn and O atoms does not exist in the MOCVD process, while it does exist in the sputtering process. When the growth temperature is low, e.g., 400 °C and 600 °C, the simulated spectra are well coincident with the experimental results, and the edges of the element steps are very sharp. However, when the growth temperature increases up to 650 °C, the edge becomes a little biased, which indicates that the high growth temperature reinforces the thermal diffusion of the atoms in the interface between the Si substrate and the ZnO epitaxial film.

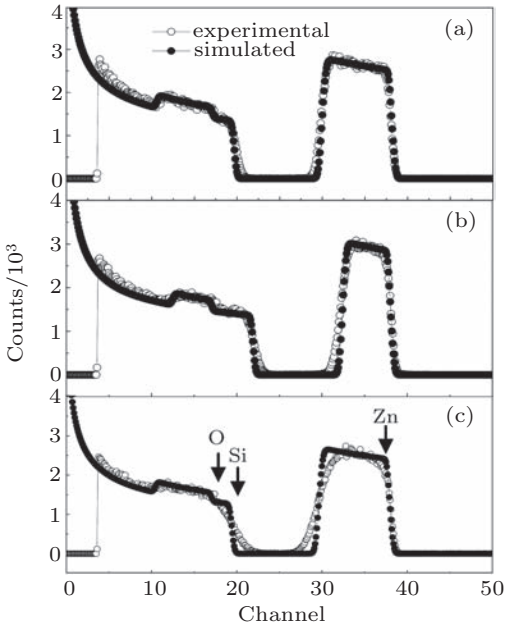


Fig. 3. RBS spectra of ZnO films grown at (a) 400 °C, (b) 600 °C, and (c) 650 °C.

XPS is commonly used to investigate the chemical state of O 1s in ZnO films. According to the result reported in the literature, the O 1s state in the ZnO film often exhibits three components, i.e., low binding energy peak (LP), middle binding energy peak (MP), and high binding energy peak (HP), nearly centred at 530.15 eV, 531.25 eV, and 532.40 eV, respectively.[17] Different locations always correspond to different chemical environments. For the above mentioned three peaks, they are attributed to O^{2-} ions in the wurtzite structure of the hexagonal Zn^{2+} ion arrays, in the oxygen deficient regions, and in the chemisorbed oxygen regions, respectively.[18] After about 50 nm surface sputtering by Ar ions, the O 1s spectra are obtained and shown in Fig. 4. All the O spectra are asymmetric (circle line). After being fitted with the Gauss method (solid lines), they are divided into three peaks, nearly consistent with LP, MP, and HP positions described above. For sample

A, the intensity of LP is very weak and the intensities of MP and HP are comparatively strong, which illuminate that most of the oxygen atoms exist in oxygen deficient and interstitial states, while a few of them are in the intrinsical sites each with a Zn–O bond. This conclusion is consistent with the poor crystal quality verified by the XRD measurement. For sample B, the intensity of LP is dramatically enhanced, and the intensities of MP and HP are restrained. We ascribe this phenomenon to the fact that compared with 400 °C, 600 °C is more suitable for ZnO growth, because under this temperature, most of Zn and O atoms are combined into Zn–O bonds, and thus the crystal quality is improved. Meanwhile, due to the low formation energy of V_O, a few desorbed oxygen atoms can easily leave the intrinsical sites and settle at the interstitial sites, forming V_O and O_i pairs corresponding to MP and HP, respectively. If the temperature increases to 650 °C, the oxygen atom desorption process is strengthened. The O_i cannot remain there but diffuses out of the film surface. So in the XPS spectrum, only the MP is left.

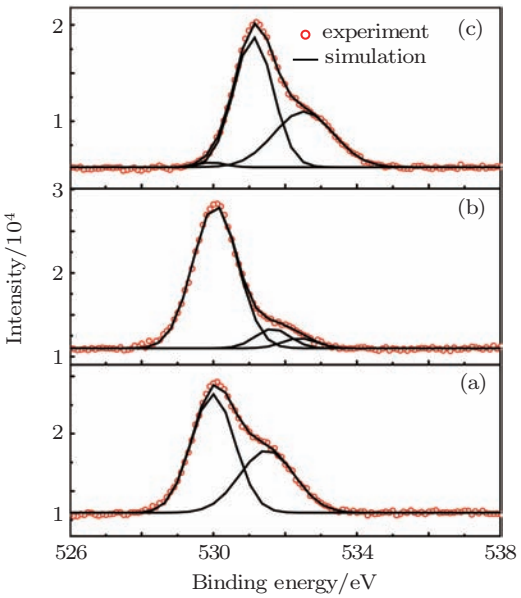


Fig. 4. (colour online) XPS spectra of ZnO films grown at (a) 400 °C, (b) 600 °C, and (c) 650 °C.

Finally, the room-temperature PL spectra of ZnO films grown at different temperatures are recorded and shown in Fig. 5. The ultraviolet emission located at about 377 nm is observed for all the samples, which originates from the radiative recombination of exciton. We can find that the film grown at high temperature has better PL properties, which is ascribed to the fact that a high growth temperature is favourable for the growth of high crystal quality films. For samples B and C, broad visible bands are also observed, which are related to V_O and O_i defects. This result is well accordant to our analysis of the XPS spectra. The intensity ratio of ultraviolet luminescence (UVL) to defect visible luminescence (DVL) is also calculated and summarized in Table 1. We can find that sample C has the highest UVL/DVL ratio.

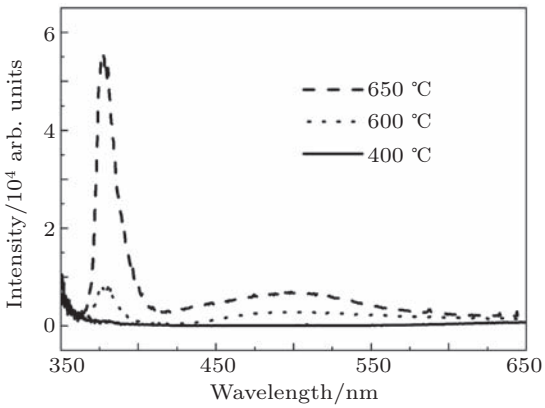


Fig. 5. PL spectra of ZnO films grown at different temperatures.

4. Conclusion

In this paper, ZnO films grown at different temperatures are prepared and characterized by SEM, XRD, RBS, and XPS. It is observed that at low growth temperature 400 °C, the ZnO film does not has a good stoichiometric ratio between Zn and O atoms and is not well crystallized. When the temperature is increased to 600 °C, the Zn/O ratio is optimized, and the crystal quality and the PL property of the film are improved. If the temperature is increased to 650 °C, the diffusion of atoms in the interface between the substrate and the epitaxial film appears, and the desorption of oxygen atoms is enhanced. Nevertheless, it has no effect on the property of the film grown at this high temperature, the film still has the best crystal quality and PL property, and especially a good intensity ratio of UVL to DVL.

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