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The effect of annealing temperature on the properties of ZnO films with preferential nonpolar plane orientation by SSCVD

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Abstract The effect of annealing temperature on the structural morphology and optical properties of preferential nonpolar plane orientated ZnO thin films on Si (100) substrates by single source chemical vapor deposition (SSCVD) was investigated. The structural and morphological properties of the films were characterized by X-ray diffraction (XRD) and atomic force microscope (AFM) measurements respectively. All the ZnO films annealed at the selected temperatures (500–800 °C) exhibiting *a–b* axis orientation, but with preferential nonpolar (100) plane orientation. It is found that the intensity of the (100) peak depends strongly on the annealing temperature, while that of (101) peak shows a variation in a very small scale. The surface morphology demonstrates that the film is of the uniform grains except for that annealed at 800 °C, for the aggregation of the ZnO particles occurred. The film shows a superior smooth surface annealed at 600 and 700 °C in comparison with other thermal annealed. It is also found from the photoluminescence(PL) measurements that the film annealed at 700 °C exhibits the lowest deep-level emission(DLE). However, the intensity of the near band edge emissions (NBE) and DLE show a wavelike variation, which are consistent to the variation of the intensity of (100) peak in the XRD results.

Introduction

ZnO is a promising material for light emitters in the UV region. Compared to other wide bandgap semiconductors, ZnO has a larger exciton binding energy (60 meV) [1], which provides more efficient excitonic emissions at room temperature. Thus the fabrication of ZnO thin films has attracted considerable attention. There are many different deposition techniques, such as molecular beam epitaxy (MBE) [2], sputtering [3], pulsed laser deposition (PLD) [4], metal organic chemical vapor deposition (MOCVD) [5, 6], atomic layer deposition (ALD), [7, 8] and also a novel single source chemical vapor deposition (SSCVD) [9, 10, 11]. But according to the reports, the ZnO thin films are always fabricated with polar *c*-axis orientation. The polar ZnO can induce electric fields along the growth direction and resulted in quantum confined Stark effect (QCSE) and poor transition probability, which is harmful for light emitting device applications. Therefore, nonpolar films are needed for future applications of ZnO for light emitting devices. Among these methods, SSCVD technology is promising to fabricated non-polar ZnO thin films using a single solid organic zinc source as precursor. Different precursors used may result in the different crystal orientation of ZnO thin films.

In general, thermal annealing is an important tool to modify the properties of films, and the crystal and optical properties of the films are always improved for the efficiency of LED or LDs. There are many reports about the effects of annealing on the *c*-axis orientation ZnO films, but little research on *a–b* axis orientation ZnO films. In this study, we fabricated *a–b* axis orientation ZnO thin films on silicon (100) substrates using a single solid organic zinc source ($Zn_4(OH)_2(O_2CCH_3)_6 \cdot 2H_2O$) by SSCVD technology, and investigated the effect of annealing temperature

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on the structural morphology and optical properties of the films.

Experiment

The ZnO thin films deposition was performed in the SSCVD system as reported [9]. The base pressure for the system was 1.5×10^{-5} Torr. During the deposition, the precursor sublimated from a resistively heated Knudsen cell with a temperature of 220 °C and the silicon (100) substrates with the temperature 450 °C, deposited for about 45 min. Then the films were inserted into a furnace and annealed at various temperatures between 500 and 800 °C in air for an hour, then cooled to room temperature naturally inside the furnace. All the films with uniform thickness of about 500 nm were examined by the cross-section of scanning electron microscopy.

The crystalline structures of the ZnO thin films annealed were investigated using a Philips X-ray diffraction (XRD) apparatus with CuKα radiation (0.15408 nm) in the θ–2θ mode, the surface morphologies were characterized by a Dimension-3000 atomic force microscope (AFM), and the PL of the films were measured at room temperature by the fluorescence spectrophotometer (SHIMADZU, RF-5301PC) using a Xe lamp (150 W) as a light source, and the exciton wavelength was chosen to be 340 nm.

Results and discussion

XRD profiles of the ZnO thin films on silicon substrates annealed at various temperatures are shown in Fig. 1. It is found that all the films have a polycrystalline hexagonal wurtzite structure with (100) and (101) orientation [12], i.e., *a*–*b* axis orientation. But all show the preferential nonpolar (100) and relatively weak (101) orientation. Table 1 shows the intensity value and the ratio ($I_{(100)}/I_{(101)}$) of the two peaks at different annealed temperatures, the RMS roughness of the film is also listed for discussion as following: At the annealing temperature range of 500–700 °C, the intensity of the (100) peak increases and then decreases with increasing temperature. While temperature increased to 800 °C, it increases again. Although the intensity of the (101) peak varies in a similar manner, it varies in a very small scale in contrast with (100) peak. These results are also proved by the variety trend of the ratio ($I_{(100)}/I_{(101)}$) with the annealing temperature as displayed in Fig. 3, the ratio increases from 3.11 at 500 °C to 4.30 at 800 °C, but with value of 4.13 at 600 °C, then decreases to 3.76 at 700 °C, just as the variety trend of the intensity of (100) peak. It indicates that the intensity of the (100) peak and the ratio of $I_{(100)}/I_{(101)}$ depends strongly on the annealing temperature, which shows the dominant difference from that of *c*-axis orientation ZnO thin film [13, 14]. And it is also interestingly found that the similar behavior can be observed in the variety of NBE and DLE intensity, as shown in the PL spectra will be discussed.

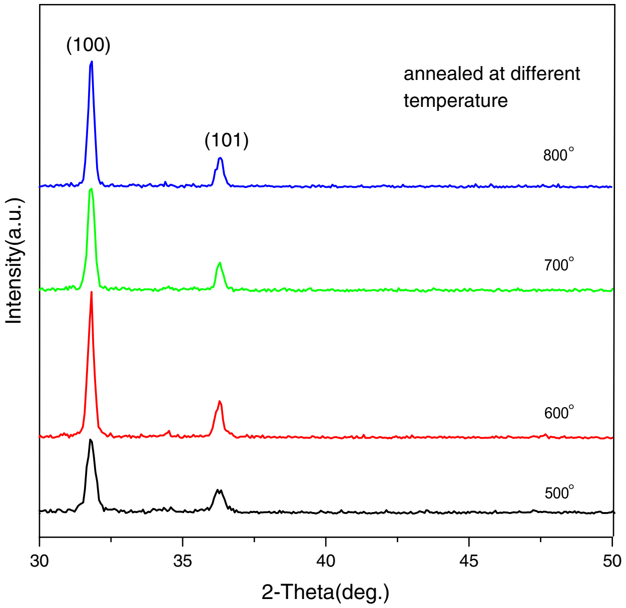


Fig. 1 XRD patterns for ZnO films annealed at various temperatures

Tapping mode AFM was used to study the surface structure of the films. Figure 2 presents the surface morphologies of ZnO thin films with various annealing temperatures. It is observed that the grains are uniformly grown and distributed with the annealing temperatures from 500 to 700 °C. But as the temperature increases to 800 °C, there appears the aggregation of particles, this phenomenon can be attributed to a thermally activated coarsening process arising when excess thermal energy supplied [15, 16]. And the AFM study also reveals the influence of annealing on the surface roughness of the films, the roughness value is listed in Table 1, with the data accuracy of ±2%. Figure 3 shows that RMS

Table 1 Annealing effect on XRD parameters and RMS roughness of surface morphology

ZnO film	$I_{(100)}$	$I_{(101)}$	$I_{(100)}/I_{(101)}$	RMS (nm)
Annealing temperature (°C)				
500	312.59	100.40	3.11	16.31
600	624.75	151.23	4.13	10.41
700	436.36	115.83	3.76	10.05
800	539.65	125.42	4.30	15.22

roughness of the films as a function of annealing temperature, the roughness decreases between 500 and 600 °C, is constant or so at 600 and 700 °C, and sharply increases at 800 °C.

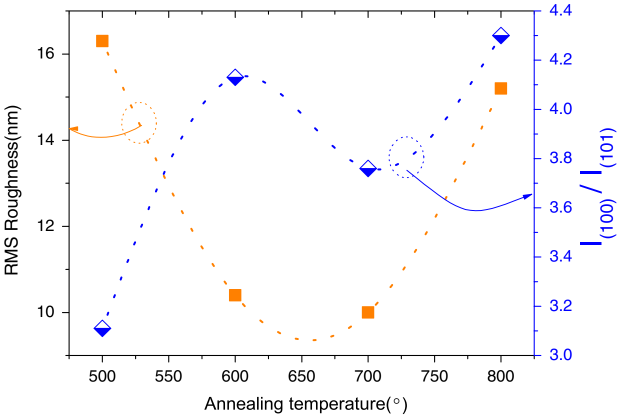
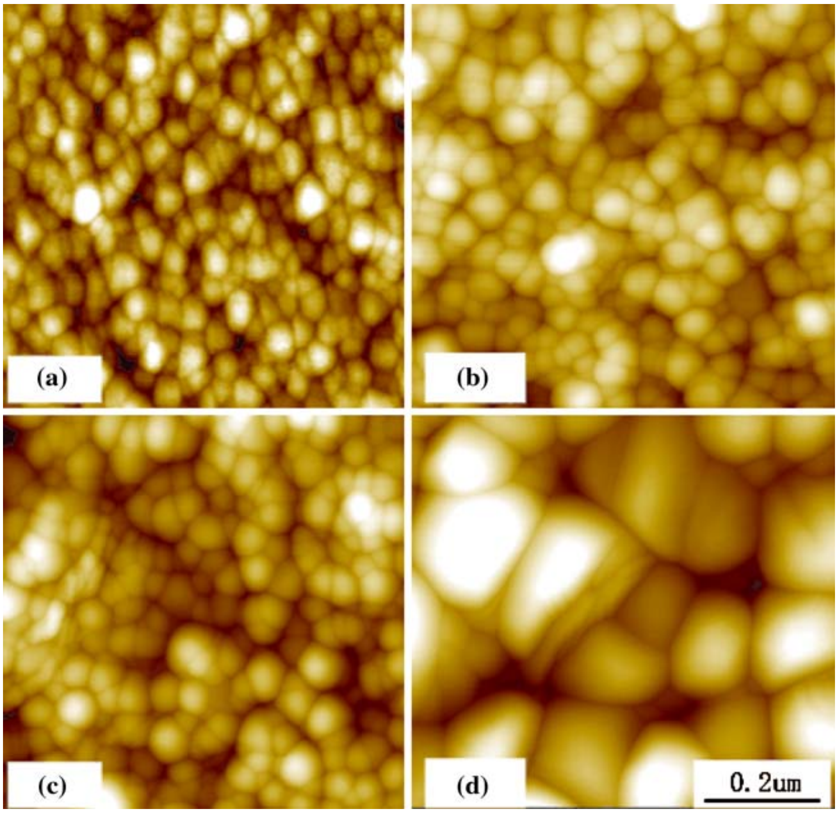


Fig. 3 Annealing effect on RMS roughness and XRD parameters ($I_{(100)}/I_{(101)}$) of ZnO films

The annealing effect on the ZnO films was also investigated by room temperature PL measurement. Figure 4 shows the PL characteristics of the films at the selected annealing temperatures, a UV NBE peak around 387 nm and a broad DLE band located in the visible region at the low energy part are observed. The NBE corresponds to the exciton emission, the intensity of the NBE increases and then decreases with increasing temperature in range (500–700 °C), then increases at 800 °C, the insert in Fig. 4 is the magnified NBE peak, the intensity of which varying with the annealing temperature is consistent to the variation trend of the intensity of (100) peak in the XRD results. A similar manner observed in DLE, while the DLE of ZnO thin film is located in the visible region of a broad blue luminescence band, which is different from the reports about *c*-axis orientation ZnO film always with DLE of green luminescence [17]. The broad blue emission band is always believed to come from intrinsic or dopant-induced defects in ZnO [18], and the blue PL curve at 600 °C shifted upward much contrast with other three curves, may attribute to that the special annealing temperature can induce defects. And it is found from the PL measurements that the film annealed at 700 °C exhibits the weakest DLE peak. However, the DLE related defects cannot be removed by annealing, as the temperature increases to 800 °C, the PL peak in the broad blue luminescence region increases along with the NBE again, this phenomenon suggests that the DLE related defects can be suppressed, also can be favored through annealing. The variation of the UV and visible emission intensity may be attributed to the annealing temperature effect on the structure of ZnO films.

Fig. 2 AFM images of ZnO films annealed at different temperatures: (**a**) 500 °C, (**b**) 600 °C, (**c**) 700 °C, (**d**) 800 °C



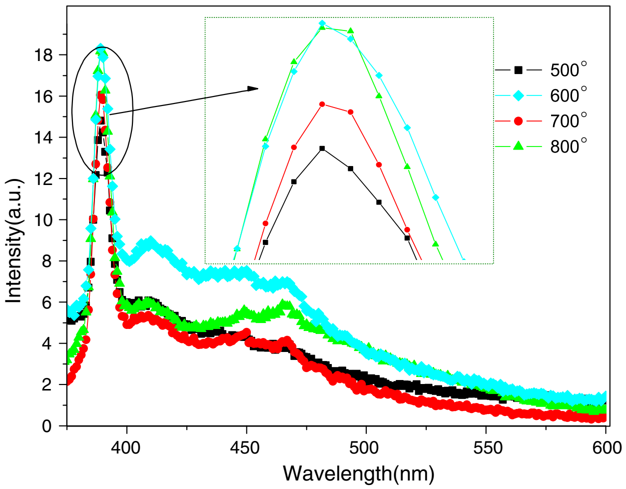


Fig. 4 PL spectra of ZnO films annealed at various temperatures, the insert is the magnified UV peak

Conclusions

In this article, the influence of annealing on the properties of preferential nonpolar plane orientation ZnO thin films was presented. The results reveal that the intensity of diffraction peak of nonpolar (100) plane depends strongly on the annealing temperature, while that of (101) peak show variation in a very small scale at the selected annealing temperatures, which is also proved by the variation of the ratio of $I_{(100)}/I_{(101)}$. It is clearly found that annealing can change the surface structure and surface morphology, the film shows the uniform grains except for annealed at 800 °C, for the aggregation of the ZnO particles in high temperature. And the surface roughness of ZnO thin film decreases with increasing temperature, but the surface morphology becomes worse as increased to 800 °C.The effects of annealing temperature on the films structure are some causes for the variation in the optical properties. It is observed from the PL measurements that the film annealed at 700 °C exhibits the smallest DLE. However, the intensity of the UV NBE shows a wavelike variation, which is consistent to the variation of the intensity of (100) peak in the XRD results. It is deduced that the properties of *a–b* axis orientation ZnO thin film strongly depend on the annealing temperature, which shows the dominant difference from that of *c*-axis orientation ZnO thin film. Thus, the study of thermal annealing is significant for modifying the properties of preferential nonpolar plane orientation ZnO films, and for further improving the efficiency of optoelectronic devices.

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References

1. Ye ZZ, Ma DW, He Jh et al (2003) J Cryst Growth 256:78
2. Bagnall D, Chen Y, Zhu Z, Yao T, Koyama S, Shen M, Golo T (1997) Appl Phys Lett 70:2230
3. Lu YM, Hwang WS, Liu WY, Yang JS (2001) Mater Chem Phys 72:269
4. Cao H, Wu JY, Ong HC, Dai UY, Chang RPH (1999) Appl Phys lett 73:572
5. Gorla C, Emanetoglu N, Liang S, Mayo W, Lu Y, Wraback M, Shen H (2000) J Appl Phys 85:2595
6. Sang B, Kushiya K, Okumura D, Yamase O (2001) Sol Energy Mater Sol Cells 67:237
7. Rugge A, Becker JS, Gordon RG, Tolbert SH (2003) Nano Lett 3:1293
8. King JS, Neff CW, Summers CJ, Park W, Blomquist S, Forsythe E, Morton D (2003) Appl Phys Lett 83:2566
9. Petrella AJ, Deng H, Roberts NK, Lamb RN (2002) Chem Mater 14(10):4339
10. Deng H, Gong B, Petrella AJ, Russell JJ, Lamb RN (2003) Sci China, Ser E 46(4):355
11. Deng H, Russell JJ, Lanb RN et al (2004) Thin Solid Films 458:43
12. Zhang XT, Liu YC, Zhang LG, Zhang JY et al (2002) J Appl Phys 92:3293
13. Fang ZB, Yan ZJ, Tan YS, Liu XQ, Wang YY (2005) Appl Surf Sci 241:303
14. Yang WZ, Zhong HL, Jie Z, Jie S, Jun WZ (2005) Vacuum 78:53
15. Lifshitz IM, Slyozov VV (1961) J Phys Chem Solids 19:35
16. Tan ST, Sun XW, Zhang XH, Chua SJ, Chen BJ, Teo CC (2006) J Appl Phys 100:033502
17. Vanheusden K, Seager CH, Warren WL, Tallant DR, Voigt JA (1999) Appl Phys Lett 68:403
18. Zhang SB, Wei SH, Zunger A (2001) Phys Rev B 63:075205