Effects of Thickness on Properties of ZnO Films Grown on Si by MOCVD

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Abstract: High quality ZnO films are successfully grown on Si(100) substrates by metal-organic chemical vapor deposition at 300 ℃. The effects of the thickness of the ZnO films on crystal structure, surface morphology, and optical properties are investigated using X-ray diffraction, scanning probe microscopy, and photoluminescence spectra, respectively. It is shown that the ZnO films grown on Si substrates have a highly-preferential *C*-axis orientation, but it is difficult to obtain the better structural and optical properties of the ZnO films with the increasing of thickness. It is maybe due to that the grain size and the growth model are changed in the growth process.

Key words: metal-organic chemical vapor deposition; X-ray diffraction; zinc compound; photoluminescence spectrum

PACC: 7360F; 8140T; 7855E

CLC number: TN304.2$^+$1 **Document code:** A **Article ID:** 0253-4177(2005)11-2069-05

1 Introduction

Zinc oxide(ZnO) is a kind of Ⅱ-Ⅵ compound semiconductor with wurtzite structure, and has a wide band gap, high exciton binding energy, excellent chemical stabilities[1,2], and outstanding physical properties. These lead to its application in many promising optoelectronic devices, such as light-emitting diodes, laser diodes, and solar cells[3~5]. ZnO films have been grown by various techniques including magnetron sputtering, chemical vapor deposition, pulsed laser deposition, and molecular beam epitaxy[6~9]. Metal-organic chemical vapor deposition (MOCVD) is a useful method for the formation of films, providing the advantages of high growth rate, larger area uniformity, and different ambience in the situ doping process[10,11]. Although sapphire substrates have been widely used to grow ZnO films, Si substrate has many advantages due to its low cost, large wafer size, and the possibility of integrating nitride semiconductors with the highly matured Si technology. The Si (100) plane is extensively used in devices and integrated technology. However, the large lattice and thermal expansion coefficient mismatch between Si and ZnO causes the direct growth of ZnO on Si substrate to be very difficult.

In this paper, ZnO films were directly grown on Si (100) by MOCVD at 300 ℃ and the relationship between the thickness, the crystal structure, and the optical properties of the films was investigated by XRD, SPM, and PL spectra. In our experiment, the ZnO films crack when the film thickness reaches about 600nm. For preparation ZnO devices, we want to obtain ZnO film with enough thickness. So we choose film thickness ranging from 174 to 462nm.

2 Experiment

ZnO films were deposited on Si (100) substrates by MOCVD. The apparatus for the deposition is shown in Fig. 1. Before epitaxy, the sub-

Received 11 March 2005, revised manuscript received 8 June 2005

strates were subjected to chemical treatment. Firstly, the Si (100) substrates were cleaned with deionized water for 5min. Then, the surface oxidized layer was etched by dipping in H_2SO_4 for 10min, NH_3 : H_2O_2 (1 : 1) for 10min, and HCl : H_2O_2 (1 : 1) for 10min. Finally, the substrates were treated in 5 % HF solution and blown in dry nitrogen gas.

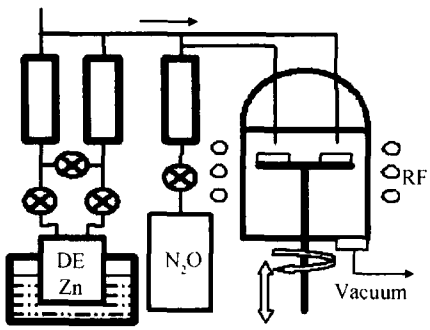

Fig. 1 Schematic diagram of MOCVD apparatus

$Zn(C_2H_5)_2$ (DEZn) and N_2O were used as the zinc and the oxygen sources, respectively. The substrate temperature was kept at 300 ℃ in this study. It is known that half of the decomposition temperature of DEZn is 280 ℃[12]. Due to that, the N_2O cannot produce unstable peroxide with DEZn during the reaction process and can more easily control the parasitic reaction than other oxygen sources, such as O_2, so N_2O is chosen as the oxygen source. The reaction of DEZn and N_2O can be expressed as follows:

$$R\text{-}Zn\text{-}R + N_2O \rightarrow R\text{-}Zn\text{-}O\text{-}R + N_2 \quad (1)$$

$$R\text{-}Zn\text{-}O\text{-}R + N_2O \rightarrow R\text{-}O\text{-}Zn\text{-}O\text{-}R + N_2 \quad (2)$$

The reaction rate of Eq. (2) is lower than Eq. (1), and the end product is alkoxide (R - O - Zn - O - R). We suggest that these reactions can be produced at low temperatures. Generally, the volatility of alkoxide is much lower than that of alkly metal (R - Zn - O - R). Therefore the pre-reaction products are the alkly metal and the further product is alkoxide. The alkoxide further thermal decomposition product is ZnO. But, the detail of these reactions is unclear at this moment and further study is needed to elucidate the mechanism. Ultra-high-purity Ar was used as the carrier gas of Zn-$(C_2H_5)_2$. The Ar flow was 60sccm and the N_2O flow was 100sccm. The pressure of the chamber is about 2.67kPa.

Three samples were grown with different thicknesses, as Table 1 shows. The thickness was measured using a surface profiler (Alpha-step 200). The crystal structure of samples was studied by XRD. Surface morphology of samples was measured by SPM. Photoluminescence (PL) measurements were carried out using a He-Cd laser at 325nm at room temperature. The excitation power of the laser was 3.4mW.

Table 1 Growth time and thickness of the samples

Sample	A	B	C
Growth time/ min	45	90	120
Thickness/ nm	174	346	462

3 Results and discussion

To investigate the crystalline properties of the three samples, XRD analysis was made. As shown in Fig. 2, all samples exhibit one ZnO (0002) peak at about $2\theta = 34.4°$, indicating that the hexagonal wurtzite structure is predominant in ZnO films. Those results show that the samples are all highly *C*-axis oriented. The position of (0002) peak slightly shifts to a higher angle direction from sample A to sample C. The full width at half maximum (FWHM) of samples A, B, and C is 0.37°, 0.35°, and 0.46°, respectively. Generally, the narrower FWHM obtained from samples A and B indicates that they have better crystal quality. The crystal quality of sample C did not improve with increasing thickness. We suggest that, with the thickness increasing, the grain is grown up and is in nucleation with a three-dimensional growth model, leading to a rough surface, which agrees with the SPM results.

SPM measurements were performed to study the difference of the surface morphology among samples A, B, and C. The images are shown in Fig. 3 over a scale of 5μm ×5μm. All samples show a

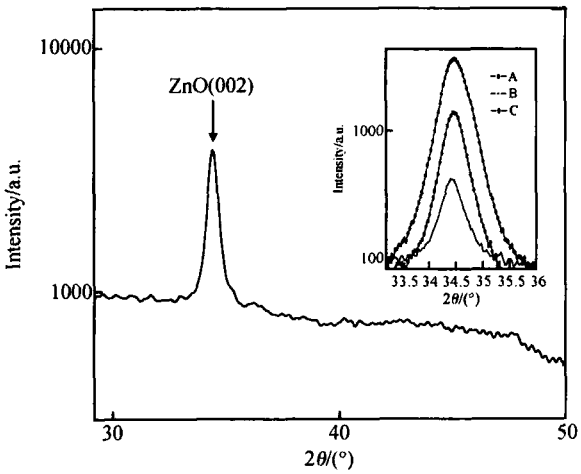

Fig. 2 XRD patterns of samples A ,B ,and C

rough surface ,which varies with the different film thicknesses. In addition ,the films surface has several large grains in Fig. 3(a) . With the further increase of thickness , the films growth becomes column by column and the grains become bigger [Figs. 3(b) and (c)]. In SPM analysis ,the root mean square (rms) roughness of samples A ,B ,and C are 6. 64 , 8. 48 , and 15. 44nm , respectively. Therefore ,sample A has the smallest rms roughness while sample C has the biggest rms roughness. We suggest that at the initial deposition stage ,the roughness surface of sample A expedites the grain coalescence ,resulting in better crystalline quality of ZnO film with a smooth surface[13] . With the film thickness increasing ,the stress is released and higher densities of nucleation occur , large quantity columns are formed and grains become bigger. We surmise that the films are grown along the *C*-axis with different deposition levels and deposited with a non-uniform film surface. Therefore ,the rms roughness increases. In addition ,the rms roughness is decreased with the film thickness decreasing ,and is very close to the crystallinity of films and the morphologies of growing films[14] .

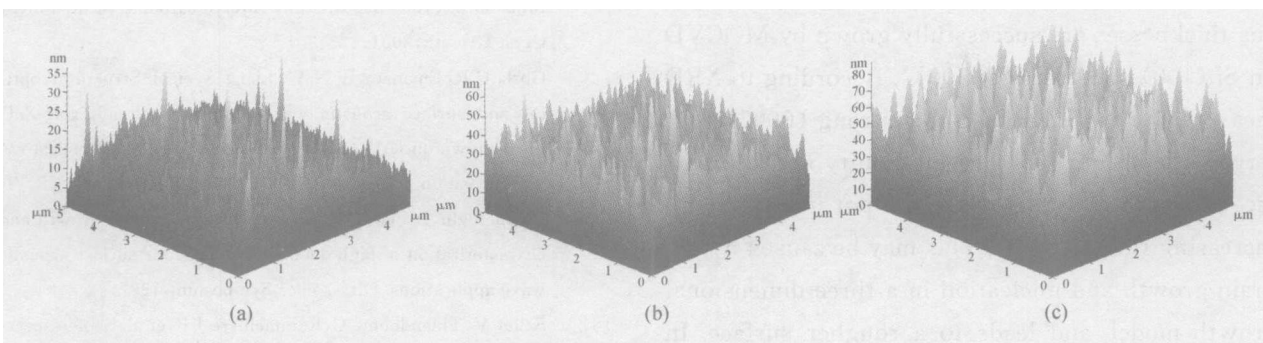

Fig. 3 SPM patterns of samples A ,B ,and C

To evaluate the luminescence properties of ZnO films , the intensity ratio of the near-band-edge-emission (NBE) to the deep-level-edge (DLE) shown in Fig. 4 was investigated at room temperature. Strong ultraviolet (UV) emission (NBE) peaks were observed at 366. 5 ,373. 1 ,and 373. 9nm , respectively , for samples A , B , and C. The UV emission PL is related to the microcrystalline structure as reported by Tang *et al*. [15] . It is well known that the NBE corresponds to the recombination of excitons bound to donors[16 ,17] . The origin of the DLE may be attributed to structural defects or impurities unintentionally introduced during the film deposition[18] . There are very weak green emissions (centered approximately at 490nm) in the PL spectra ,which indicates that all the samples have good optical properties. The FWHM of the UV emission peak of samples A ,B , and C are 16. 97 ,16. 76 ,and 22. 85nm ,respectively. They become wider with increasing film thickness from sample B to sample C. Therefore , samples A and B have better optical quality due to their narrower FWHM than sample C. And the red shift of UV emission peak can be observed from samples B ,C to sample A. The shift is probably caused by the quantum confinement effect[19] . So we surmise

the red shift and the broadening of the UV peak may be due to the localization in the ZnO films ,and the bigger grain size ,which is consistent with the SPM results.

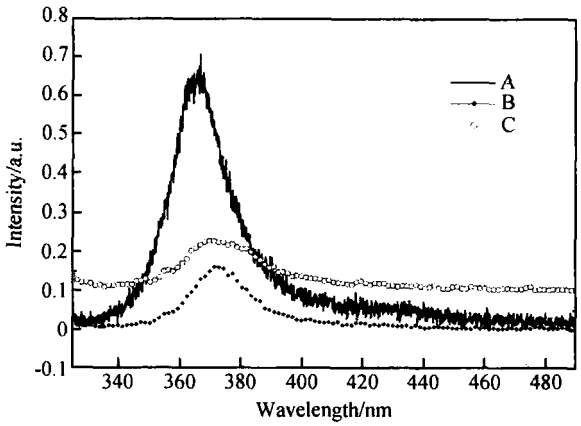

Fig. 4 PL spectra of samples A ,B ,and C

4 Conclusion

In summary ,high-quality ZnO films with various thicknesses are successfully grown by MOCVD on Si (100) substrates at 300 ℃. According to XRD measurement ,all samples show strong (0002) preferred orientation. The crystal quality and the surface morphology of sample C did not improve with increasing the thickness. This may be caused by the grain growth and nucleation in a three-dimensional growth model ,and leads to a rougher surface. In PL spectra ,one strong UV luminescence and a very weak DL E are observed in all samples. But ,the optical properties of sample C is also not improved with increasing the thickness because the biggest FWHM of NBE. Moreover ,the red shift of the UV emission peak is also consistent with the SPM results. It is demonstrated that it is still difficult to grow thick ZnO films with a better crystal structure and better optical properties in our experiment range.

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厚度对 Si 衬底上生长的 ZnO 薄膜性能的影响

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摘要：采用金属有机化学气相沉积方法，在 Si(100)衬底上生长出具有高度 *C* 轴择优取向的 ZnO 薄膜. 通过 X 射线衍射、原子力显微镜和室温光致发光谱研究了厚度对 ZnO 薄膜的结构、表面和光学性能的影响. X 射线衍射图显示 ZnO 薄膜只有单一的(0002)峰，具有高度择优取向. AFM 和 PL 测试表明，在取样薄膜厚度范围内，薄膜的表面质量和发光性能没有随着薄膜厚度的增加而提高. 这是因为薄膜在厚度增加的生长过程中，生长模型变化且晶粒增大.

关键词：金属有机化学气相沉积；X 射线衍射；锌化合物；光致发光谱

PACC：7360F；8140T；7855E

中图分类号：TN304.2^{+}1　　**文献标识码**：A　　**文章编号**：0253-4177(2005)11-2069-05

2005-03-11 收到，2005-06-08 定稿