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ZnO Films Grown by the Vapor Transport Method

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Abstract: The characterizations of surface morphologies, crystal structures, and optical properties of the ZnO films prepared by a vapour-phase technique on different substrates were performed in this study. Scanning electron microscopy (SEM) data showed that larger ZnO particles are formed on the Au-covered Si substrates than those on Si substrates. X-ray diffraction (XRD) results indicated that hexagonal wurtzite ZnO films are grown on both Si(111) and Si(100) substrates though they present different diffraction peaks with hexagonal wurtzite structure, while appears no sphalerite structure. The ZnO films prepared on Au-coated Si substrates prefer to grow along with *c*-axis orientation. The PL spectra reveal only a narrow strong UV emission peak at about 389 nm (3.19 eV) in all the ZnO samples.

Key words: ZnO; thin film; vapor transport; water vapor
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1 Introduction

In recent years, ZnO, as a wide band gap semiconductor, has attracted much attention on studying its growth mechanism and electrical and optoelectronic properties due to a variety of applications in electronic, photoelectronic and spintronic devices. ZnO has a stable hexagonal wurtzite structure in the space group $P6_3mc$ with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm. Its large exciton binding energy (60 meV), which is much greater than the thermal energy at room temperature (RT), makes it a promising candidate for applications in blue-UV light emission and RT UV lasing[1]. Furthermore, ZnO can be used as a highly transparent electrode material for solar cells[2], a phosphor material for converting radiation to visible light at low voltages[3], a piezoelectric material in mechanical transducers and a gas-detection material for microsensors due to its unique electronic properties, piezoelectricity, and surface chemistry sensitive to environment.

Various fabrication techniques have been established for the growth of thin ZnO films and nanostructures, such as the molecular beam epitaxy (MBE)[4,5], chemical vapor deposition[6,7], vapor-phase growth[8~10], aqueous solution growth[11], electrochemical deposition[12], carbonthermal evaporation[13], flux growth and template-based synthesis[14]. We synthesized ZnO films using a vapor transfer method. The Zn powders with high purity and H_2O vapor were employed as the sources. After heated at above 800 ℃ and below 1 180 ℃, the Zn powders will be transferred to gas phase Zn vapor, thus the reaction equation can be written as following,

$$Zn(g) + H_2O(g) \xrightarrow{<1\,180\ ℃} ZnO(s) + H_2(g).$$

Different nanostructures of ZnO films were synthesized on different substrates. Morphologies of the grown ZnO films were imaged by scanning electron microscopy (SEM). Films' crystal structures and optical properties were then characterized by X-ray diffraction (XRD) and photoluminescence (PL) spectrum, respectively.

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2 Experiments

The reactions of the vapor-phase growth took place in a large quartz tube horizontally lain down in a rapid thermal furnace. For the purpose of controlling the stable pressure and the high efficient use of the Zn powders during ZnO synthesis, another much smaller quartz tube placed in the large quartz tube was used to create a zinc-rich environment during the growth of ZnO. Fig. 1 shows the schematic illustration of the furnace including a horizontal quartz tube of about 2 m in length and 20 cm in diameter, and a smaller quartz tube of 15 cm in length and 3 cm in diameter located in the middle of the bigger quartz tube. The huge difference in size between these two tubes will provide a stable Zn vapor pressure during ZnO deposition. The Zn powders and the substrates were placed with a distance of about 0.5 cm in the smaller quartz tube. In this experiment, mirror-polished p-type silicon wafers of 25 mm in diameter, such as Si(111) and Si(100), cleaned by acetone and alcohol, were used as substrates. SiO_2/Si(100) surface was prepared by oxidizing the clean Si(100) wafer with the alternation of dry and wet O_2 to form about 500 nm SiO_2 layer. The Au covered Si(100) and SiO_2/Si(100) substrates were prepared by depositing a 200 nm thick layer of Au on the cleaned Si(100) and SiO_2/Si(100) wafers using RF-sputtering (JC500-3/D) with a gold target.

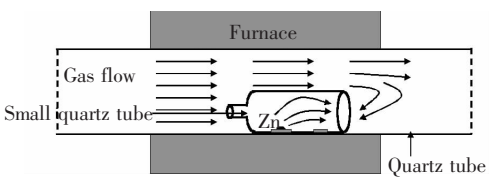

Fig. 1 The schematic illustration of the vapor-growth system with a large horizontal quartz tube placed in a furnace and a smaller quartz tube inside the big quartz tube

The synthesis procedures were carried out in the following steps: first, nitrogen gas was flown through the quartz tubes for 1 h in order to drive away the impure gases; second, the furnace temperature was elevated to 800 ℃ in 1 h with nitrogen gas flying; third, the temperature was maintained at 800 ℃ for 1 h with the flow of nitrogen gas mixed H_2O vapor; finally, the furnace was switched off and the samples were cooled down to RT.

The morphologies of the nanostructures were characterized by using a LEO-1530FE-SEM. The crystal structures were analyzed by XRD within the 2θ range of 20° ~ 80° at a scan rate of 0.0167°/step, using PANalytical X'pert PRO X-ray diffractor with Cu/Mo radiation source. PL measurements were taken at RT using a KrF excimer laser line of 248 nm as the excitation source by a Hitachi F-4500 spectrophotometer.

3 Results and Discussion

The morphologies of ZnO films deposited on different substrates at 800 ℃ are shown in Fig. 2. It is found that the ZnO films grown on Si(111) [Fig. 2(a)] and Si(100) [Fig. 2(b)] substrates are more smooth. Strip shape ZnO particles with different sizes and orientations can be observed. This implies that the growth of ZnO has no any dominate direction on the Si(111) and Si(100) substrates in this study. For ZnO grown on Au-coated Si(100) and SiO_2/Si(100) substrates, circle-like-on-top nanoparticles can be found in Fig. 2(c) and (d). The size is about 10 to 200 nm in diameter. The nanoparticles labeled as M are flat, labeled as N are gyroidal, and the extremely bright spot labeled as H can be assigned

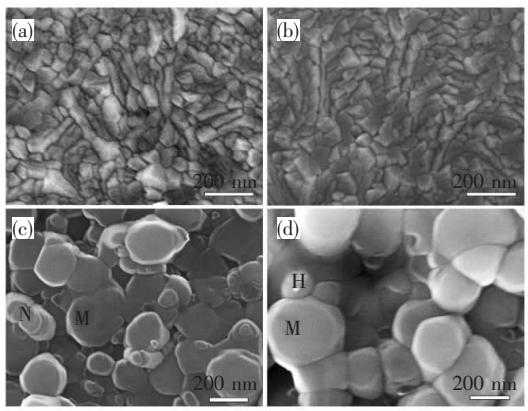

Fig. 2 The SEM images of ZnO films grown on (a) Si(111), (b) Si(100), (c) Au-coated Si(100), and (d) Au-coated SiO_2/Si(100) substrates at 800 ℃ for 1 h.

as a nucleating clusters. By comparing the SEM images in Fig. 2, it can be found that the average size of the nanoparticles in Fig. 2(c) and (d) is larger than that in Fig. 2(a) and (b). This suggests that the ZnO growth rate on the Au covered Si substrates is faster than that on the Si substrates due to the catalysis effect of Au.

The influence of the substrate on the ZnO crystal structure is depicted in Fig. 3. It is clear that substrate plays an important role in determining the crystal structure of the ZnO films. The films deposited on Si(111) has a polycrystalline structure with a (002) preferred orientation. Secondary peaks present are (100), (101), (102), (110) and (103). All these diffraction peaks can be indexed to a pure hexagonal wurtzite ZnO structure. The film deposited on Si(100) has two dominate ZnO peaks: (002) and (200). The ZnO films grown on the Au covered Si substrates have the most dominate peak at around 34° assigned to the (002) plane diffraction peak besides Au (111), (200) and (220) peaks at around 38°, 45°, and 65°, respectively. This result indicates that the ZnO films grown with Au catalysis are highly orientated in *c*-axis along [0001] direction. Unfortunately, the use of metal catalyst for the growth of ZnO films makes the presence of unwanted impurities inevitable. Additionally, the appearances of Si related diffraction peaks are believed from Si substrates. The variations in crystal structure among those samples on different substrates might be due to the different surface diffusion energies, and atomic structure of these substrates, which affect the surface diffusion and adsorption of the reactants (e. g. Zn and H_2O) as well as their reaction rate. More detailed study is needed to be performed in order to clearly understand the substrate influences on the crystal structure.

The optical properties of all synthesized ZnO

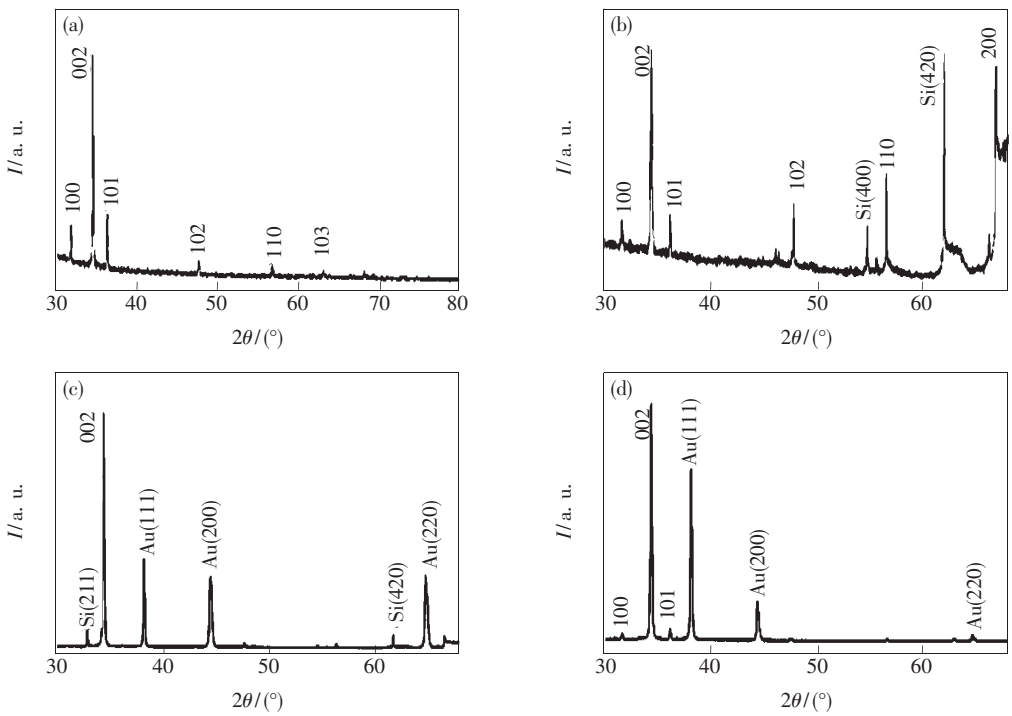

Fig. 3　The XRD patterns of ZnO films grown on (a) Si(111), (b) Si(100), (c) Au-coated Si(100), and (d) Au-coated SiO_2/Si(100) substrates.

samples are displayed by PL spectrum (seen in Fig. 4). Expect for the difference in peak intensity, it is interesting to find that all RT PL spectra of the ZnO samples consist of only a narrow strong UV peak at around 389 nm (3.19 eV) in wavelength. The UV emission band is attributed to a near band-edge excitonic transition of ZnO[15]. While there is no green emission peak, which is related to some deep level

transition induced by defects, e. g. oxygen vacancies[16] (e. g. single ionized oxygen vacancies) or impurities. Thus, ZnO synthesized through the vapor method in this study is highly crystalline with few defects and impurities.

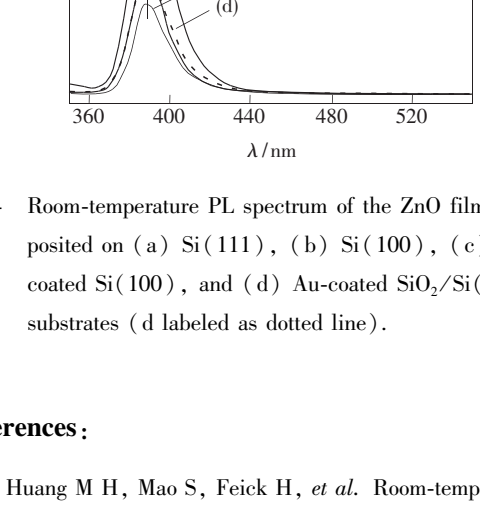

Fig. 4 Room-temperature PL spectrum of the ZnO films deposited on (a) Si(111), (b) Si(100), (c) Au-coated Si(100), and (d) Au-coated SiO_2/Si(100) substrates (d labeled as dotted line).

4 Conclusion

The ZnO films were synthesized by reaction of Zn vapor and H_2O vapor using a vapor-phase technique on different substrates. Films' surface morphologies, crystal structures, and optical properties were investigated. The SEM data suggested that higher growth rate is found on the Au covered substrates. XRD studies indicated that the growth orientation of ZnO strongly depends on the substrates. ZnO films grown on Si(111) or Si(100) substrates presents different diffraction peaks in hexagonal wurtzite structure, while appears no sphalerite structure. The ZnO films grown on Au-coated Si substrates prefer to grow along *c*-axis orientation. The PL spectra with showing only a narrow strong UV emission peak reveal few defects and impurities in the synthesized ZnO films.

References:

[1] Huang M H, Mao S, Feick H, *et al.* Room-temperature ultraviolet nanowire nanolasers [J]. *Science*, 2001, **292**(5523): 1897-1899.

[2] Morgan J H, Brodie D E. The preparation and some properties of transparent conducting ZnO for use in solar-cells [J]. *Can. J. Phys.*, 1982, **60**(10): 1387-1390.

[3] Vanheusden K, Seager C H, Warren W L, *et al.* Correlation between photoluminescence and oxygen vacancies in ZnO phosphors [J]. *Appl. Phys. Lett.*, 1996, **68**(3): 403-405.

[4] Li H, Sang J P, Liu C, *et al.* Microstructural study of MBE-grown ZnO film on GaN/sapphire (0001) substrate [J]. *Centr. Eur. J. Phys.*, 2008, **6**(3): 638-642.

[5] Su Shichen, Lu Youming, Zhang Zhenzhong, *et al.* Structural and optical properties of high quality $Mg_xZn_{1-x}O$ films grown by P-MBE [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(2): 309-312 (in Chinese).

[6] Li Z Y, Xu F C, Wu Q H, *et al.* Zinc oxide thin film synthesized by combustion chemical vapor deposition [J]. *Appl. Sur. Sci.*, 2008, **255**(5): 2859-2863.

[7] Tian Ke, Shi Yuanyuan, Xu Xiaoqiu, *et al.* The investigation of growth orientation of ZnO films by CVD [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(2): 294-298 (in Chinese).

[8] Mycielski A, Kowalczyk L, Szadkowski A, *et al.* The chemical vapour transport growth of ZnO single crystals [J]. *J. Alloys Compd*, 2004, **371**(1-2): 150-152.

[9] Ntep J M, Hassani S S, Lusson A, *et al.* ZnO growth by chemical vapour transport [J]. *J. Cryst. Growth*, 1999, **207**(1-2): 30-34.

[10] Shiloh M, Gutman J. Growth of ZnO single crystals by chemical vapour transport [J]. *J. Cryst. Growth*, 1971, **11**(2): 105-107.

[11] Li J, Srinivasan S, He G N, *et al.* Synthesis and luminescence properties of ZnO nanostructures produced by the sol-gel method [J]. *J. Cryst. Growth*, 2008, **310**(3): 599-603.

[12] Xu F, Lu Y N, Xia L L, *et al.* Seed layer-free electrodeposition of well-aligned ZnO submicron rod arrays via a simple aqueous electrolyte [J]. *Mater. Res. Bull.*, 2009, **44**(8): 1700-1708.

[13] Janfeshan B, Bahrevar M, Ahmadi K. ZnO nanorods grown by carbothermal evaporation [J]. *Internat. J. Modern Phys.*,

B, 2008, **22**(18-19):3289-3295.

[14] Deng S, Fan H M, Zhang X, *et al*. An effective surface-enhanced Raman scattering template based on a Ag nancluster-ZnO nanowire array [J]. *Nanotech.*, 2009, **20**(17):175705-1-7.

[15] Zhang Y, Jia H B, Yu D P, *et al*. Low-temperature growth and Raman scattering study of vertically aligned ZnO nanowires on Si substrate [J]. *Appl. Phys. Lett.*, 2003, **83**(22):4631-4633.

[16] Vanheusden K, Warren W L, Seager C H, *et al*. Mechanisms behind green photoluminescence in ZnO phosphor powders [J]. *J. Appl. Phys.*, 1996, **79**(10):7983-1990.

气相输运法制备 ZnO 薄膜

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摘要: 运用气相输运技术在不同的衬底上制备 ZnO 薄膜,同时对这些 ZnO 薄膜的表面形貌、晶体结构和光学特性进行表征。在扫描电子显微镜图像上可以看到,相比没有镀金的 Si 衬底,ZnO 纳米颗粒在镀金的 Si 衬底上的生长尺寸较大。X 射线衍射测试结果表明,在 Si(111)和 Si(100)衬底上生长的 ZnO 薄膜显示出不同的六角纤锌矿结构的衍射峰,但没有出现立方闪锌矿 ZnO 结构的衍射峰。在镀金的 Si 衬底上,ZnO 薄膜生长取向主要为 *c* 轴方向。此外,所有 ZnO 样品的光致发光谱上均只出现一个狭窄且强的紫外峰,约在 389 nm (3.19 eV)波长处。

关　键　词: ZnO; 薄膜; 气相输运; 水蒸气
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