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Effects of Substrate on the Structure, Morphology and Optical Properties of Vertically Aligned ZnO Nanorod Arrays Grown by Low-temperature CBD Method

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Abstract: ZnO nanorods were grown on different substrates (quartz glass, Si and ITO glass) by the wet chemical bath deposition (CBD) method at a relatively low temperature of 95℃. X-ray diffraction (XRD) and scanning electron microscope (SEM) results illustrate that the ZnO nanorod arrays with hexagonal wurtzite structure are grown densely and vertically on all the substrates, whereas the average diameter and length are found to be closely related to the substrates nature. High intensity near-band edge ultraviolet (UV) emission peak are observed in room temperature photoluminescence (PL) spectra for the ZnO nanorod arrays on all substrates, yet the usually observed defect related deep level emissions are nearly undetectable regardless of crystalline or amorphous, indicating high optical quality ZnO nanorod arrays can be achieved *via* this low temperature easy process chemical approach. Moreover, the small shift in the UV emission among different substrates is interpreted in terms of compress stress, which is further demonstrated by the Raman spectra measurement results.

Key words: ZnO; nanorod arrays; chemical bath deposition; photoluminescence

The interest in ZnO structures has increased drastically in recent years because of their potential applications in nanoelectronic devices such as field-effect transistors[1], single-electron transistors[2], photodiodes[3], and chemical sensors[4]. Some novel and fascinating ZnO nanostructures have been reported, such as nanowires, nanorods and nanotubes, core-shell hybrid particles[5], hollow spheres[6], and dandelions[7]. Among these 1D nanomaterials, ZnO is a wide band gap semiconductor and one of the most versatile materials. On account of its various remarkable properties, such as a wide band gap (3.37eV), a large exciton binding energy (60meV), excellent chemical and thermal stability, transparency, biocompatibility, and wide electrical conductivity range, ZnO nanomaterials are of global interest currently and has a variety of applications in an emerging area of nanotechnology[8]. ZnO is probably the richest family of nanostructures among all materials, which exhibit the most splendid and abundant configurations of nanostructures that one material can form. An up-to-date comprehensive review on ZnO nanomaterial platform for nanotechnology can be found in Ref [9]. For the technological applications of ZnO nanorods, rational synthesis and fundamental understanding about their properties are essential. Up to now, numerous experimental attempts have been reported to fabricate ZnO nanoscale materials, such as molecular beam epitaxy (MBE)[10], pulsed laser deposition (PLD)[11], sputtering[12], electrochemical deposition[13], vapor phase transport (VPT)[14], chemical vapor deposition (CVD)[15], thermal evaporation[16]. Compared with the methods mentioned above, the wet chemical bath deposition (CBD) method as a high performance growth technique for ZnO nanorods/nanowires has recently received increasing attraction due to its obvious advantages of low-cost, low temperature operation and environmental friendliness. The effects of growth parameters such as precursor concentration, growth temperature and growth time have been investigated extensively and well established[17]. A key issue in this field is the choice of substrate, therefore, an understanding of the effects of substrate on the structure and optical properties of ZnO nanorods will benefit the realization of nano-ZnO based applications by this high performance growth technique.

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formance growth technique.

In this paper, the wet CBD method was employed to fabricate ZnO nanorods with special attention paid to the effects of the substrates on the structure, morphology and optical properties of as-grown ZnO nanorods. It should be noted that only strong near-band edge UV emission peak were observed in room temperature PL spectra for the ZnO nanorod arrays on all substrates regardless of crystalline or amorphous, yet the usually observed defect related deep level emissions were nearly undetectable, indicating high optical quality ZnO nanorod arrays could be achieved *via* this low temperature easy process chemical approach. The high optical quality ZnO nanorod arrays presented here is very prospective for its applications in optoelectronic nanodevices, such as UV lasers, light- emitting diodes, and vertical field effect transistor arrays.

1 Experimental

CBD technique has been proved to be a good approach for synthesis of ZnO nanorods with the use of ZnO seeds in the form of thin films or nanoparticles[18]. Here, quartz, single crystal Si (111) and ITO glass were chosen as substrates for ZnO nanorod arrays grown using a CBD technique. To investigate the effect of substrate on the properties of ZnO nanorods, a series of experiments were performed for different substrates under the constant growth parameters. The substrates were cleaned in the ultrasonic bath with methylbenzene, acetone, ethanol and deionized water, respectively to remove adsorbed dust and surface contamination. Then, the Si substrate was etched by 2% HF solution to get rid of the residual oxide layer. In order to fabricate vertically aligned nanorods, a 30nm thick seed layer was fabricated on the substrates by radio-frequency (RF) magnetron sputtering. 50mL aqueous solutions composed of 0.02mol/L zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 98%) and hexamethylenetetramine (HMT) ($C_6H_{12}N_4$, 99%) were used as precursor source for the growth of ZnO nanorods. The molar ratio of $Zn(CH_3COO)_2{\cdot}2H_2O$ and HMT was kept to be 1: 1. The solution was then transferred into a sealed glass bottle in which the substrates were suspended vertically. The sealed bottle was subsequently put into an oven kept at 95℃ for 5h. All the growth parameters (precursor concentration, growth temperature and time) have been optimized for obtaining a high aspect ratio and well-defined hexagonal prism shape of the ZnO nanorods. At the end of the growth, the substrates were taken out of the solution and rinsed several times with deionized water, and blew dried with high purity N_2 gas at room temperature. A detailed chemistry process by CBD technique can be found elsewhere[19].

The crystal structure and morphology of the as-grown ZnO nanorods were investigated by X-ray diffraction (XRD) on Bruker Axs D8, scanning electron microscope (SEM) on HITACHI S-4800. To investigate the optical properties, PL measurements were performed at room temperature using a He-Cd laser with an excitation wavelength of 325 nm. Raman spectra measurements were carried out on Raman spectrometer (Renishaw Invia, UK) equipped with inverse microscope (ZEISS Axiovert 25).

2 Results and discussion

2.1 Chemical process of CBD technique for the growth of ZnO nanorods

The chemical process involved in the growth of ZnO nanorods can be described as follows: $Zn(CH_3COO)_2{\cdot}2H_2O$ provides Zn^{2+} ions required for building up ZnO nanorods, water molecules in the solution provide O^{2-} ions. Even though the exact function of HMT during the growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH^-[20]. The detailed chemical reactions were:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (1)$$

$$H_2O + NH_3 \leftrightarrow OH^- + NH_4^+ \quad (2)$$

$$Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \text{ or}$$

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow Zn(OH)_2(NH_3)_4 \quad (4)$$

$$Zn(OH)_2/\,Zn(OH)_2(NH_3)_4 \rightarrow ZnO + H_2O \quad (5)$$

The growth process of CBD can be controlled through the five chemical reactions listed above. All of the five reactions can be controlled by adjusting the reaction parameters, such as precursor concentration, growth temperature and growth time. With the movement of the reaction equilibrium to the right side, ZnO will form through dehydration of $Zn(OH)_2$ and precipitate onto the substrates.

2.2 Effects of substrate on structure characters and morphology of ZnO nanorods

Figure 1 shows the XRD patterns of ZnO nanorods grown on three kinds of substrates, (a) quartz glass substrate, (b) Si substrate and (c) ITO glass substrate. All diffraction peaks are consistent with the wurtzite structure, which can be indexed to a standard spectrum of JCPDS (No, 36-1451). For all the samples, the (002) diffraction peak in XRD patterns is dominant, yet other peaks are nearly invisible, which reveals the preferentially oriented growth in the c-axis direction. In addition, it can be found that the (002) peak intensity for the samples deposited on quartz glass and Si substrates are much higher than that of

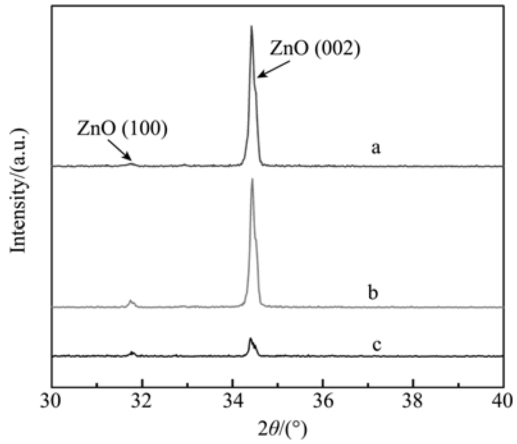

Fig. 1　XRD patterns of ZnO nanorods grown on different kinds of substrates
(a) Quartz glass; (b) Si; (c) ITO glass

samples deposited on ITO glass substrate, which was suggested to be caused by the less amount of ZnO nanorods grown on the ITO glass than that on the quartz and Si substrates.

Figure 2 shows the SEM images of as-grown samples grown on three kinds of substrates. It can be clearly observed from the figures that the ZnO well-defined nanorod arrays were successfully grown densely and vertically on all the substrates. However, the average diameter and length of the ZnO nanorods array were closely related to the substrate nature. The length and average diameter of the ZnO nanorods on the quartz glass, Si and ITO glass were 3.3um (120nm in average diameter), 2.5um (105nm in average diameter), and 2.3um (60nm in average diameter), respectively. Thus, the aspect ratios on the quartz glass, Si and ITO glass were calculated to be 27.5, 23.5, and 38.3, respectively. It has been well established that the higher average density and length of the nanorods will lead to higher intensity of the (002) diffraction peak[21]. Therefore, the SEM results were in well agreement with the results of XRD characterization. The effects of substrate on the structure and morphology of ZnO nanorods may be understood from the nucleation and growth process[22]. The structure and morphology of ZnO nanorods was to a large extent decided by the number of nuclei formed at the very beginning of the growth, which continued to grow and form nanorods. The main differences of substrates lie in the lattice structure, defects and surface chemistries on the substrate surface, which were considered to be important factors in the nucleation and growth[23]. Among the three substrates, ITO glass presents the largest crystal lattice mismatch with ZnO compared with the single crystal of Si and quartz, as a result, ZnO nanorod arrays with less uniformity and poor preferred orientation were obtained for the samples grown on ITO glass.

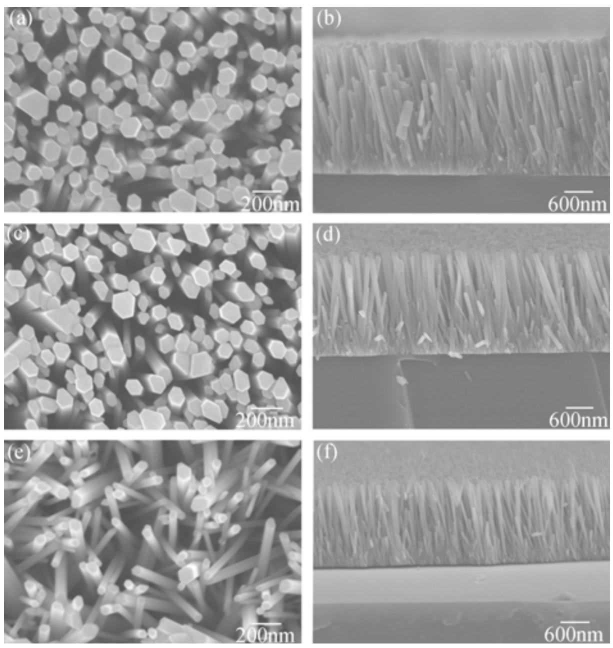

Fig. 2　SEM images of as-grown samples grown on three kinds of substrates
(a) (b) Quartz glass; (c) (d) Si; (e) (f) ITO glass

2.3　Effect of substrates on optical properties of ZnO nanorods

Optical properties of nanorods are important for many of their technological applications. Figure 3 shows the room temperature PL spectra of ZnO nanorods grown on different substrates with the same condition. The UV emission in ZnO PL spectra is well accepted as the near band edge emission which has an exciton nature[24-26]. Meanwhike, the visible emission band in ZnO PL spectra is usually observed for most ZnO nanorods reported in literature, which is believed to be closely related to the defect level induced by the defects of O vacancies, Zn interstitials or their complexes[27-28]. In our case, however, it should be noted that only strong near-band edge UV emission peak at about 380nm were observed for the ZnO nanorod arrays on all substrates regardless of crystalline or amorphous, yet the usually observed defect related deep level emissions were nearly undetectable, indicating high optical quality ZnO nanorod arrays were successfully achieved *via* this low temperature easy process chemical approach. It is also shown from Fig.3 that the UV peak intensity of sample (c) is remarkably lower than sample (a) and (b), indicating relatively poor optical quality for the ZnO nanorods grown on ITO glass substrate. Compared with the samples on ITO substrates, a slight red shift in UV emission is observed for ZnO nanorods grown on quartz and Si substrates, which is assumed to be associated with the different compress stress in the ZnO nanorods. That is, a big compress stress will result in the narrowing of the band gap and further lead to the red shift of

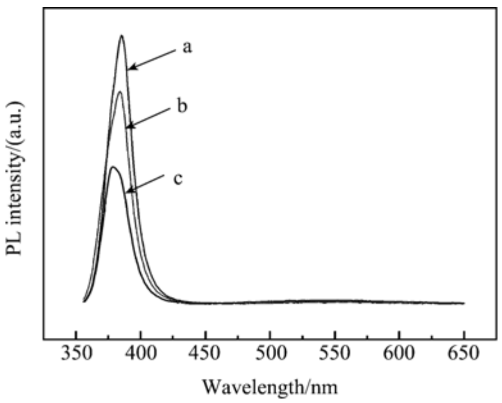

Fig. 3 PL spectra of ZnO nanorods grown on different substrates with the same condition
(a) Quartz glass; (b) Si; (c) ITO glass

near band edge emission[29].This assumption will be demonstrated by Raman spectra measurements.

Raman scattering spectrum is very useful and sensitive for determining crystal perfection and structural defects. Wurtzite ZnO crystal has two formula units in the primitive cell and belongs to C_6^4 space group[30]. According to the group theory, single-crystalline ZnO has eight sets of optical phonon modes at Γ point of the Brillouin zone. Based on the group analysis, $A_1+E_1+2E_2$ are Raman active. Both A_1 and E_1 modes are polar and splited into transverse optical (TO) and longitudinal optical (LO) phonons. According to the selection rule, E_2 and LO are Raman active, while the E_1 and TO are forbidden. Figure 4 shows the Raman spectra at the range of 100–900cm^{-1} for ZnO nanorods grown on different substrates. The peak located at 303.5cm^{-1} and 520.5cm^{-1} are Si vibration modes. And the peaks for three kinds of samples are located at 441cm^{-1} (grown on quartz substrate), 440.6cm^{-1} (grown on Si substrate), and 437.8cm^{-1} (grown on ITO glass substrate), respectively. These peaks in Raman spectra are E_2 (high) mode, which are the intrinsic characteristic of the Raman active mode of wurtzite hexagonal ZnO[31]. Therefore, the results from Raman spectrum measurements are in good agreement with the XRD and SEM analysis. In addition, the peaks of E_1(LO) are not detected for all the samples, which have been regarded to be associated with the defects of O vacancies, Zn interstitials or their complexes (580 cm^{-1})[32]. This should be the reason why the defect level induced visible emission band were absent in our ZnO nanorods PL spectra. Moreover, a Raman upshift of 0.8-4.0 cm^{-1} can be observed compared with the frequency of the E_2(high) mode in ZnO standard sample (437.0cm^{-1}), indicating a compressive stress exist in our ZnO nanorods samples[33]. The maximum and minimum compress stress are found for samples grown on the quartz substrate and on the ITO glass substrate, respectively, such

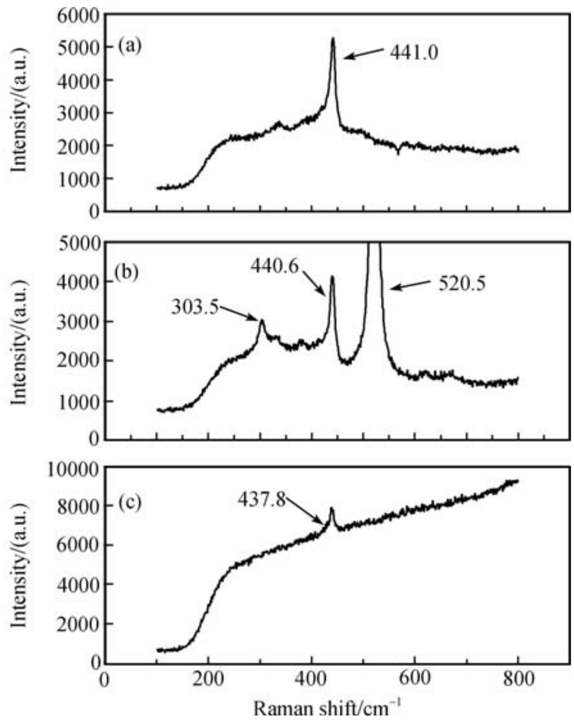

Fig. 4 Raman spectra of ZnO nanorods grown on different substrates
(a) Quartz glass substrate; (b) Si substrate; (c) ITO glass

behaviors are in accord with the above mentioned slight shifts in UV emission of PL spectra. The compress stress should be associated with the lattice mismatch between the substrate and ZnO nanorods, as well as the nature of the substrate.

3 Conclusions

ZnO nanorod arrays were successfully synthesized on different substrates by the wet chemical bath deposition (CBD) method. Effects of the substrate on the structure, morphology and optical properties of ZnO nanorods were studied. XRD and SEM results demonstrate that the ZnO nanorod arrays with a hexagonal wurtzite structure were grown densely and vertically on all the substrates, whereas the average diameter and length were found to be closely related to the substrates nature. It should be noted that only strong near-band edge UV emission peaks were observed in room temperature PL spectra for the ZnO nanorod arrays on all substrates, yet the usually observed defects related deep level emissions were nearly undetectable regardless crystalline or amorphous, indicating high optical quality ZnO nanorod arrays could be achieved *via* this low temperature easy process chemical approach. The high optical quality ZnO nanorod arrays presented here was very prospective for its applications in optoelectronic nanodevices, such as UV lasers, light-emitting diodes, and vertical field effect transistor arrays.

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衬底对低温化学池沉积法生长的垂直 ZnO 纳米棒阵列的结构、形态和光学性能的影响

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摘 要: 衬底的选择是得到高质量 ZnO 纳米棒的一个重要因素. 在 95℃的较低温度下用 CBD 方法在不同衬底(石英玻璃, 硅和 ITO 玻璃)上生长 ZnO 纳米棒阵列. X 射线衍射(XRD)和扫描电镜 (SEM)结果显示六角形的 ZnO 纳米棒致密垂直地生长在衬底上, 而纳米棒的平均直径和长度则与衬底的性质密切相关. 各种衬底的 ZnO 纳米棒阵列的室温光致发光(PL)光谱都可以观测到强烈的近带边紫外发射峰, 而无论是晶体还是非晶体, 经常可以观察到的与缺陷相关的深能级发射都几乎观察不到. 这意味着通过这种简便的低温化学方法可以获得高光学性能的 ZnO 纳米棒阵列. 此外, 不同衬底间 UV 发射的小幅度迁移可以用压应力来解释, 并用拉曼光谱进行了进一步的证明.

关 键 词: ZnO; 纳米棒阵列; 化学池沉积法; 光致发光

中图分类号: TB34 **文献标识码:** A