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Effects of substrate on morphologies and photoluminescence properties of ZnO nanorods

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ABSTRACT

Zinc oxide (ZnO) nanorods were grown on three kinds of substrates (Si, glass and ITO-conducting glass) by the chemical solution deposition method (CBD) in an aqueous solution that contained zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and methenamine ($C_6H_{12}N_4$). The nature of the substrate was found to have effect on the crystal structure, morphologies and photoluminescence properties of the resultant ZnO nanorods. From the X-ray measurement results, it can be seen that the growth orientation of the resultant ZnO nanorods deposited on various substrates were (0 0 2), but the highest intensity of (0 0 2) diffraction peak appeared in the samples deposited on glass and ITO-conducting glass compared to that of Si substrate. SEM results showed the nanorods grown on the bare glass had the most uniform size and the highest coverage density. Photoluminescence measurements were also carried out, the result showed that the ZnO nanorods grown on three kinds of substrates had different photoluminescence behaviors, and the one grown on the Si substrate had the best performance. And the small shift in the UV emission was caused by the compressive stress from the Raman measurement results.

1. Introduction

One-dimensional (1D) nanostructures such as nanorods, nanotubes and nanowires have attracted much interest because of their importance in basic scientific research and potential technological application [1]. In particular, zinc oxide (ZnO), with a wide band gap (3.37 eV), is a promising semiconductor material for applications considered for other wide bandgap materials like GaN and SiC. In addition, due to the extreme large exciton binding energy (60 meV), the excitons in ZnO are thermally stable at room temperature, and thus ZnO has significant advantages in optoelectronic applications such as the ultraviolet (UV) lasing media [2].

Until now, different fabrication methods, such as vapor-phase transport [3], pulsed laser ablation [4], chemical vapor deposition [5,6], electrochemical deposition [7] and thermal evaporation [8,9] have been widely reported for the preparation of 1D ZnO nanostructures. According to these methods, they are not suitable for controllable synthesis. Furthermore, the complex processes, sophisticated equipment and economically prohibitive high temperatures are also required. Compared with those methods, chemical solution deposition method (CBD) can be controlled easily, and no sophisticated equipments are required. The most important is that the experiment can be carried out under low temperature. In addition, little work has focused on the preparation of ZnO nanorods using different substrates, especially the effects of the substrate on the morphologies and photoluminescence properties.

Therefore, in this paper, ZnO nanorods grown on different substrates are prepared by the method of CBD just under the optimized growth condition reported in our previous paper [10]. Then the effects of different substrates on their structure, morphologies and photoluminescence properties are studied.

2. Experimental

ZnO nanorods used in the experiment were grown on Si(1 0 0) substrate, bare glass and ITO-conducting glass by the CBD process.

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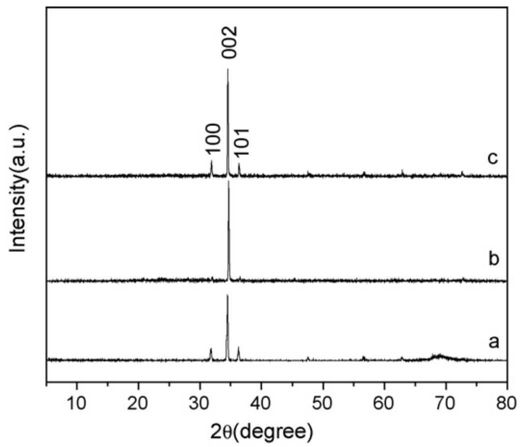

Fig. 1. XRD patterns of ZnO nanorods grown on three kinds of substrates: (a) on Si substrate, (b) on ITO-conducting glass substrate and (c) on bare glass substrate.

In the process, aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99.9% purity) and methenamine ($C_6H_{12}N_4$, 99.9% purity) was first prepared, while keeping the same 1:1 ratio (e.g., zinc nitrate hexahydrate solution (0.1 M) and methenamine solution (0.1 M)). The samples grown on different substrates were prepared with the same experimental parameters. The concentration of zinc and amine were fixed at 0.1 M, and the reaction time was 10 h.

The substrates used in the experiment were cleaned ultrasonically with acetone, ethanol and deionized water for 20 min, respectively. Then, the substrates were immersed and tilted against the wall of bottle in the precursor solution at 90 °C in an oven for 10 h without any stirring. Finally, the samples were thoroughly cooled to room temperature, washed with deionized water and dried in air.

3. Characterization

XRD (MAC Science, MXP18, Japan), SEM (Hitachi, S-570), PL (He–Cd Laser, 325 nm) and Raman (Invia-UV, UK) were used to characterize the crystal structure, surface morphologies and photoluminescence properties of ZnO nanorods.

4. Results and discussion

4.1. Effect of different substrates on morphologies of ZnO nanorods

Fig. 1 shows the XRD patterns of highly oriented ZnO nanorods grown on three kinds of substrates, (a) Si substrate, (b) ITO-conducting glass substrate and (c) bare glass substrate, which reveals the nanorods are ZnO hexagonal wurtzite structure. In comparison with the standard XRD pattern, the much higher

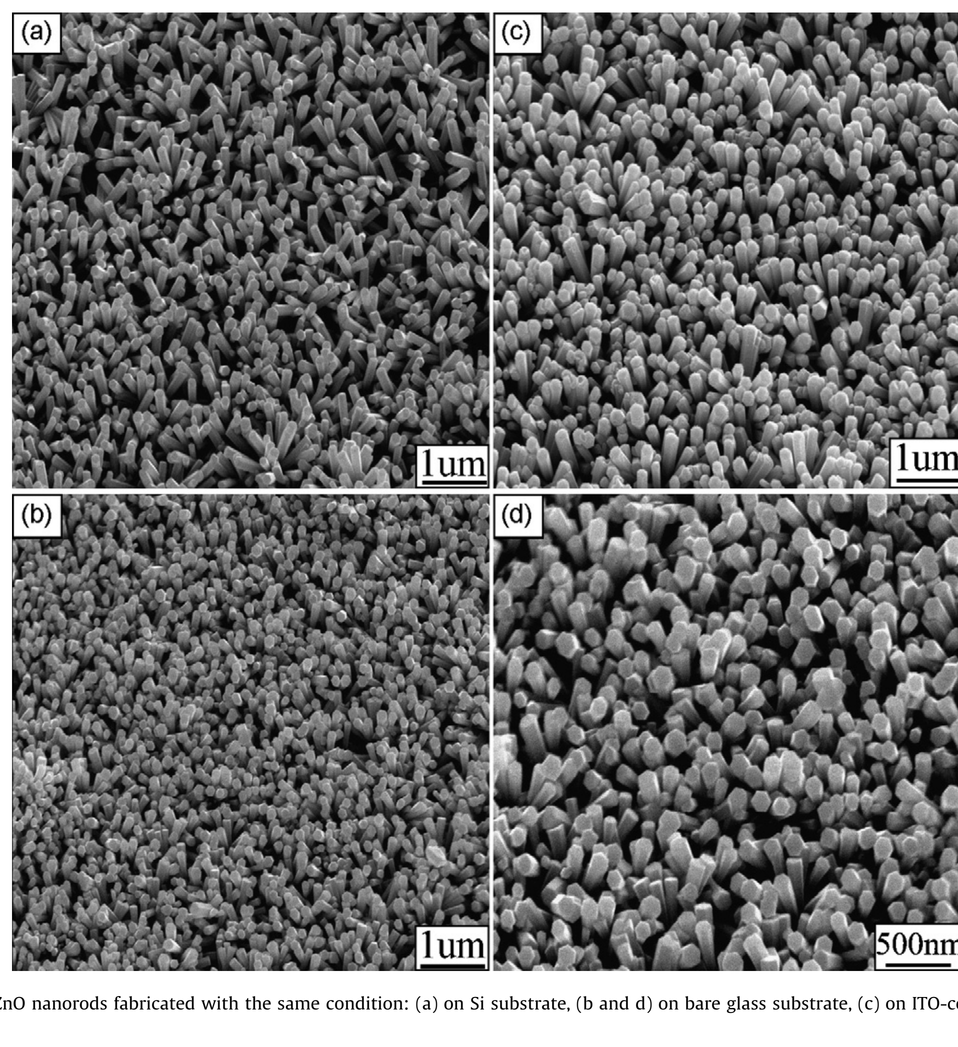

Fig. 2. SEM images of ZnO nanorods fabricated with the same condition: (a) on Si substrate, (b and d) on bare glass substrate, (c) on ITO-conducting glass substrate.

relative intensity of the (0 0 2) diffraction peak provides further evidence that the nanorods are preferentially oriented in the *c*-axis direction, which indicates that the ZnO nanorods trend to grow perpendicular to the substrate surface. However, in Fig. 1(a), the peak located at 69.1° is corresponding to Si(0 0 4) plane, which confirms the low density of nuclei and small thickness of the film on Si(1 0 0) substrate. By comparison, the (0 0 2) reflection of the pattern (b) and (c) is greatly enhanced relative to that of pattern (a).

Fig. 2 shows the SEM images of highly oriented ZnO nanorod arrays grown on different substrates. As expected, the coverage density and morphology of the ZnO nanorod arrays on the Si, glass and ITO-conducting glass are significantly different. From Fig. 2(a), it can be seen that the nanorods with an average size of 130 nm were obtained by using the Si substrate. Meanwhile, as shown in Fig. 2(c), nanorods about 150 nm by using the ITO-conducting glass were obtained and they were more uniform than that of Fig. 2(a). Compare with the two pictures, a highly uniform and densely packed array of hexagonal ZnO nanorods with the diameter of 120 nm formed over the entire glass substrate, which can be clearly seen in Fig. 2(b). And the high magnification picture shows that the nanorod array grown on the glass substrate has the most uniform size (Fig. 2(d)). In addition, the histograms of the diameter of the nanorods grown on three substrates are given in Fig. 3. From the images, it can be clearly seen that the nanorod array grown on the glass substrate has the most uniform size, and its coverage density is highest among three samples which can be determined by the numbers of nanorods in the same size area we choose randomly.

It can be explained that the different morphologies of the resultant nanorods on Si, glass and ITO-conducting glass should be related to the lattice structure and defects on the substrate surface, which is an important factor governed the chemically adsorption and subsequent nucleation and growth [10,11]. The bare glass substrate which belongs to the amorphous structure has smoother surface and less defects than the other substrates. Compared with the bare glass, the structure defects of ITO-conducting glass surface are increased because of the existence of the conducting layer. In a like manner, the lattices mismatch and more defects on Si substrate lead to the low coverage density.

Generally, the coverage density of the nanorods will affect the intensity of the (0 0 2) diffraction peak. From Figs. 2 and 3, it can be clearly seen that the intensity of the (0 0 2) diffraction peak increases with the coverage density of the nanorods. And the nanorod array grown on the bare glass has the highest coverage density, which lead to the highest intensity of the (0 0 2) diffraction peak, consistent with the conclusion of XRD. It illustrates that the lattice match and defects on the surface affect the morphology as well as crystal orientation of the resultant films.

4.2. Effect of different substrates on photoluminescence properties of ZnO nanorods

Fig. 4 illustrates the room temperature photoluminescence (PL) spectra of ZnO nanorods grown on different substrates with the same condition. As seen in Fig. 4, three luminescence emission peaks, a sharp UV emission at ∼383 nm, a weak green emission at ∼550 nm and orange emission at ∼602 nm, were observed. Generally, the UV emission must be related to the bound excitons [12–14], and the green emission was due to the point defects, such as oxygen vacancies or impurities [15]. The deep level involved in the orange luminescence was attributed to the intrinsic defect in ZnO as oxygen interstitials suggesting oxygen excessive in the sample [16], and perhaps had much to do with the structure of

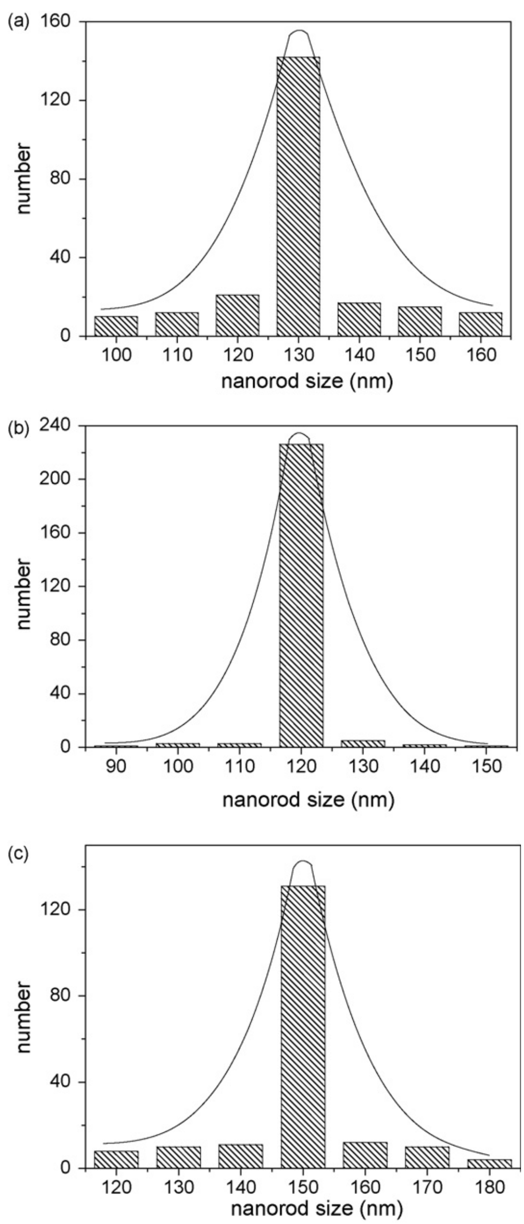

Fig. 3. The histograms of the diameter of the nanorods: (a) on Si substrate, (b) on bare glass substrate and (c) on ITO-conducting glass substrate.

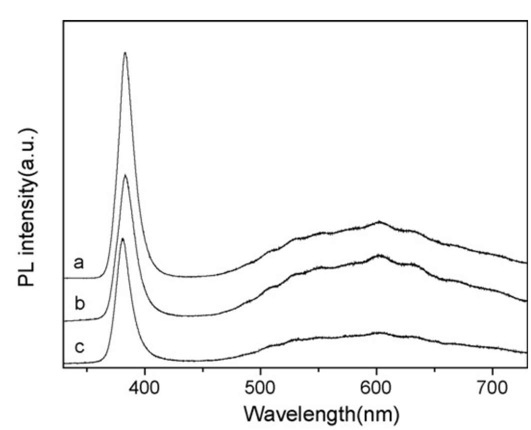

Fig. 4. PL spectra of ZnO nanorods fabricated with the same condition: (a) on Si substrate, (b) on bare glass substrate and (c) on ITO-conducting glass substrate.

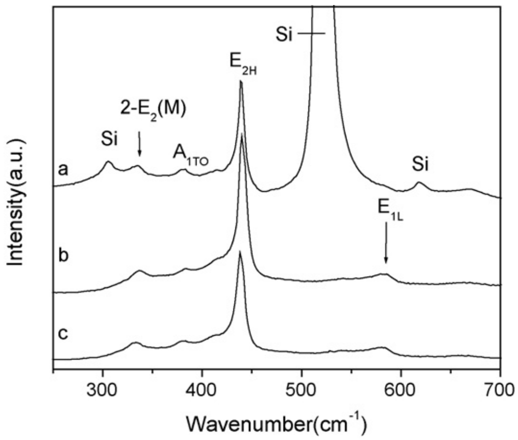

Fig. 5. Room temperature Raman spectra of ZnO nanorods fabricated with the same condition: (a) on Si substrate, (b) on bare glass substrate and (c) on ITO-conducting glass substrate.

ZnO_2 [17]. From the PL spectra of these samples, the intensity of the UV emission decreased while the green and orange emissions increased from Fig. 4(a) and (b). And the PL emission intensity in the green and orange regions gradually decreased while the UV emission intensity increased again (Fig. 4(c)). To ascertain by computation, the relative PL intensity ratio of ultraviolet emission (I_{UV}) to deep level emission (I_{DLE}) of ZnO nanorods grown on the Si substrate is estimated to be about $\sim$4.0, which is the highest among them. It indicates that its photoluminescence property is the most perfect. It can be explained that progressive increase of the UV emission relative to the deep level emission suggests the ZnO nanorods have higher crystallization and the low density of defects in the ZnO nanorods.

In addition, Fig. 4 also shows that the position of the ultraviolet (UV) peak depends on the substrates. While there can be small (0.1–2.2 nm) variations in the peak position in the spectra excited from different samples, the UV emission from sample (a) and sample (c) is in general blue shift compared to the sample (b). The slight shift in UV emission is not caused by quantum confinement because the size of nanorods is much bigger. It is possible because the stress in the ZnO nanorods films.

Raman scattering, which is very sensitive to the microstructure of materials, is used to research the stress. Wurtzite-type ZnO belongs to the space group C_{6v}^4 with two formula units in the primitive cell. The optical phonons at Γ point of the Brillouin zone belong to the following irreducible representation: $\Gamma_{opt} = 1A_1 + 2B_1 + 2E_1 + 2E_2$. Both A_1 and E_1 modes are polar and are split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active [18]. The two nonpolar E_2 modes (E_{2H} and E_{2L}) are Raman active only. The B_1 modes are infrared and Raman inactive (silent modes). Fig. 5(a)–(c) shows the Raman spectra for three samples. The peaks located at 305.6, 521.5 and 617.5 cm^{-1} are Si vibration modes. The peaks located at 335.0, 383.3, 438.2 and 580.6 cm^{-1} are assigned to second-order Raman spectrum $2 - E_2(M)$, A_{1T}, E_{2H} and E_{1L}, respectively. Previous investigations have shown the relation between the stress and the E_{2H} mode frequency: under a compressive stress the E_{2H} upshifts, whereas a tensile stress leads to a downshift of the E_{2H} mode [19]. The positions of the E_{2H} mode of three samples are observed at 438.2 cm^{-1} (grown on ITO-conducting glass substrate), 438.5 cm^{-1} (grown on Si substrate) and 439.9 cm^{-1} (grown on bare glass substrate), which shows the Raman shift (0.3–1.7 cm^{-1}) among three samples. With respect to the frequency of the E_{2H} mode in ZnO standard sample (437.0 cm^{-1}) [19], the Raman shift (1.2–2.9 cm^{-1}) is observed in the ZnO nanorods films. The upshift indicates a compressive stress in the ZnO nanorods films. By comparison, the E_{2H} upshifts (0.3–1.7 cm^{-1}) of three samples, as shown in Fig. 5, indicating an increase in the compressive stress. Probably the stress is due to the lattice mismatch or the nature of the substrate.

5. Conclusion

Well-aligned ZnO nanorods with the hexagonal wurtzite structure have been efficiently grown on three kinds of substrates (Si, glass and ITO-conducting glass) by the CBD method. The effects of different substrates on morphologies and photoluminescence properties of the resultant ZnO nanorod arrays have been investigated. This effect may be mainly concerned with the nature of the substrate, that is to say, lattice structure and defects on the substrate surface. According to the three kinds of samples, the XRD and SEM results all indicate that *c*-axis was the optimum orientation. Photoluminescence measurements show that the nanorods grown on the Si substrate have a relatively stronger UV emission than the other samples. Moreover, a compressive stress in the ZnO nanorods films results in the small shift in the UV emission among three samples. In this paper, although the morphologies and photoluminescence properties of ZnO nanorods grown on three kinds of substrates are different, it can provide a choice to grow ZnO nanorods on other substrates instead of conventional sapphire substrate. So it enables us to obtain the film device not only grown on the Si substrate but also grown on the amorphous substrate. In addition, the high electrical conductivity and optical transparency of ITO-conducting glass substrate also provide a great potential in future optoelectronic nanodevice applications.

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References

[1] (a) X. Duan, Y. Hunag, Y. Cui, J. Wang, C.M. Lieber, Nature 409 (2001) 66; (b) M.H. Huang, S. Mao, H. Feick, H. Yang, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
[2] Q.X. Zhao, M. willander, Appl. Phys. Lett. 83 (2003) 165.
[3] Y. Wu, P. Yang, Chem. Mater. 12 (2000) 605.
[4] M.H. Huang, Y. Wu, H. Feick, E. Weber, P. Yang, Adv. Mater. 13 (2001) 113.
[5] Y. Wu, R. Fan, P. Yang, Nano Lett. 2 (2002) 83.
[6] J.-J. Wu, S.-C. Liu, Adv. Mater. 14 (2002) 215.
[7] P.M. Izaki, T. Omi, J. Electrochem. Soc. 144 (1997) 1949.
[8] B.D. Yao, Y.E. Chan, N. Wang, Appl. Phys. Lett. 81 (2002) 757.
[9] J. Yang, D. Wang, L. Yang, et al. J. Alloys Compd. 450 (2008) 508.
[10] J. Yang, J. Lang, L. Yang, et al. J. Alloys Compd. 450 (2008) 521.
[11] L. Vayssieres, Adv. Mater. 15 (2003) 464.
[12] D. Weissenberger, M. Dürrschnabel, D. Gerthsen, et al. Appl. Phys. Lett. 91 (2007) 132110.
[13] W.I. Park, Y.H. Jun, S.W. Jung, et al. Appl. Phys. Lett. 82 (2003) 964.
[14] D.C. Reynolds, D.C. Look, B. Jogai, Phys. Rev. B 57 (1998) 12151.
[15] B.K. Choi, D.H. Chang, Y.S. Yoon, S.J. Kang, J. Mater. Sci. 10854 (2006) 9036.
[16] D. Li, Y.H. Leung, A.B. Djurisic, Z.T. Liu, M.H. Xie, S.L. Shi, S.J. Xu, W.K. Chan, Appl. Phys. Lett. 85 (2004) 1601.
[17] W.D. Yu, X.M. Li, X.D. Gao, P.S. Qiu, W.X. Cheng, A.L. Ding, Appl. Phys. A (2004) 2665.
[18] J.M. Calleja, M. Cardona, Phys. Rev. B 16 (1977) 3753.
[19] Y. Huang, M. Liu, Z. Li, Y. Zeng, S. Liu, Mater. Sci. Eng. B 97 (2003) 111.