Photoluminescence of ZnO nanostructures grown by the aqueous chemical growth technique

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Abstract

Zinc oxide nanostructured films were grown by the aqueous chemical growth technique using equimolar aqueous solutions of zinc nitrate and hexamethylenetetramine as precursors. Silicon(100) and glass substrates were placed in Pyrex glass bottles with polypropylene autoclavable screw caps containing the precursors described above, and heated at 95 °C for several hours. X-ray diffraction $2\theta/\theta$ scans showed that the only crystallographic phase present was the hexagonal wurtzite structure. Scanning electron microscopy showed the formation of flowerlike ZnO nanostructures, consisting of hexagonal nanorods with a diameter of a few hundred nanometers. The photoluminescence spectra of the ZnO nanostructures were recorded at 18–295 K using a cw He–Cd laser (325 nm) and a pulsed laser (266 nm). The ZnO nanostructures exhibit an ultraviolet emission band centered at ∼3.192 eV in the vicinity of the band edge, which is attributed to the well-known excitonic transition in ZnO.
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1. Introduction

Zinc oxide (ZnO) is a well-studied transparent wide band-gap semiconductor ($E_g = 3.37$ eV) with a large exciton binding energy (∼60 meV), which allows efficient excitonic emission at

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room temperature (RT) [1,2]. Therefore, ZnO appears as a major candidate for RT optoelectronic applications such as efficient short-wavelength ultraviolet light-emitting diodes and laser diodes. For one-dimensional (1D) ZnO nanostructures a stronger excitonic effect is expected due to the carrier quantum confinement in nanorods or nanowires [3]. Therefore, various chemical and physical methods have been applied for creating ZnO nanostructures. For instance, high-temperature vapor–liquid–solid (VLS) growth with the use of catalysts [4,5], pulsed laser deposition [6], electrochemical deposition in porous membranes [7], metal vapor transport using Zn sources [8], physical vapor transport using ZnO and graphite powders [9], chemical vapor deposition using zinc acetylacetonate hydrate [10], thermal oxidation of ZnS [11], metalorganic chemical vapor deposition (MOCVD) using diethylzinc and O_2 or N_2O as precursors [12] and aqueous chemical growth [13,14] have been reported amongst other techniques. Compared with other methods, aqueous chemical growth allows the synthesis of advanced nano-, meso-, and micro-particulate thin films without any template or surfactant at large scales and low cost.

In this work, we investigate the morphology, crystal structure and emission characteristics of ZnO nanostructures synthesized by the aqueous chemical growth technique on Si(100) and glass substrates. The ZnO flowerlike nanostructures consist of uniform nanorods with hexagonal cross section and exhibit high crystalline quality. They show a strong UV excitonic emission band at ∼3.192 eV, depending on the substrate used and deposition period.

2. Experimental part

ZnO nanostructures were grown by the aqueous chemical growth (ACG) technique using equimolar (0.01 M) aqueous solutions of zinc nitrate and hexamethylenetetramine as precursors. Silicon(100) wafer pieces and slide glass substrates, which were first cleaned with spectroscopic grade propanol and acetone, washed with MilliQ water and dried under N_2 gas flow, were placed in Pyrex glass bottles with polypropylene autoclavable screw caps containing the precursors described above, and heated at 95 °C for several hours (1–20 h for slide glass substrates and 1–40 h for Silicon(100) substrates). Subsequently, the substrates were thoroughly washed with MilliQ water to eliminate residual salts or amino complex, and dried in air at the same temperature.

The surface morphology of the ZnO nanostructures was examined by scanning electron microscopy (SEM), while their crystal structure was determined by X-ray diffraction (XRD) using a Rigaku diffractometer with CuKα X-rays. The photoluminescence measurements were carried out using a He–Cd cw laser at 325 nm with full power 35 mW, and a 266 nm frequency-quadrupled solid state-pumped YAG laser with 0.5 ns pulse width, 7.6 kHz repetition rate and 5 mW average power in order to excite the photoluminescence of the samples. The ZnO samples were attached to the cold finger of a closed cryostat system and cooled down to the desired temperature for measurements between 18 and 295 K. The spectra were recorded using a very sensitive LN$_2$ cooled CCD camera and a UV–visible spectrometer.

3. Results and discussion

Fig. 1(a) and (b) present typical XRD patterns of ZnO nanostructures grown for 5 h on Si(100) and glass substrates, respectively. They both exhibit sharp diffraction peaks characteristic of the ZnO wurtzite hexagonal phase (wurtzite-type, space group P6$_3$*mc*, JCPDS card file No. 36-1451), which implies that pure ZnO was formed. No characteristic diffraction peaks from other phases or impurities were detected. It was observed that by increasing the growth time on glass from 1 to 20 h, an enhancement of the (002) peak relative intensity occurs, indicating a
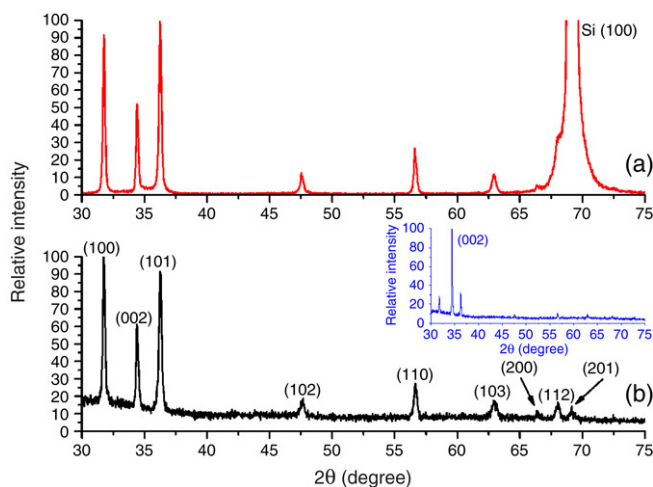
Fig. 1. XRD patterns of ZnO samples synthesized with aqueous chemical growth for 5 h on (a) Si(100) and (b) glass substrates. In the inset of (b) the XRD pattern of ZnO grown on glass for 20 h is presented.
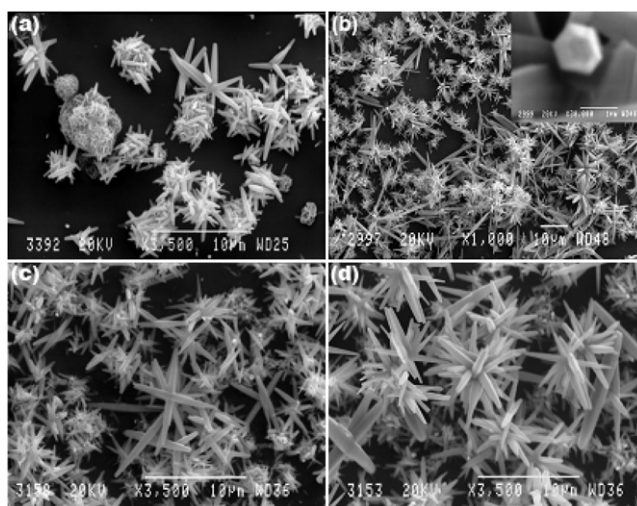

Fig. 2. SEM images of ZnO samples synthesized with aqueous chemical growth (a) 1 h on glass, (b) 20 h on glass, (c) 1 h on Si(100) and (d) 5 h on Si(100). In the inset of (b) the hexagonal shape of the ZnO nanorods is clearly observed.

preferential growth orientation along the *c*-axis for high deposition periods (inset of Fig. 1(b)). The full width at half maximum (FWHM) of the (002) diffraction peak is 0.157° for 20 h growth on glass, attesting to the high crystalline quality of the ACG nanostructured samples.

Fig. 2 shows SEM images of the ZnO nanostructures synthesized by the ACG technique. SEM micrographs of the nanostructures formed on glass substrates after 1 h and 20 h growth are presented in Figs. 2(a) and 2(b), respectively. Sponge-like structures are observed after 1 h growth, out of which uniform shaped nanorods emerge (Fig. 2(a)). However, only a partial coverage of the substrate area (∼30%–35%) could be achieved. When the growth time increases to 20 h, flowerlike architectures dominate the ZnO nanostructures (Fig. 2(b)) with
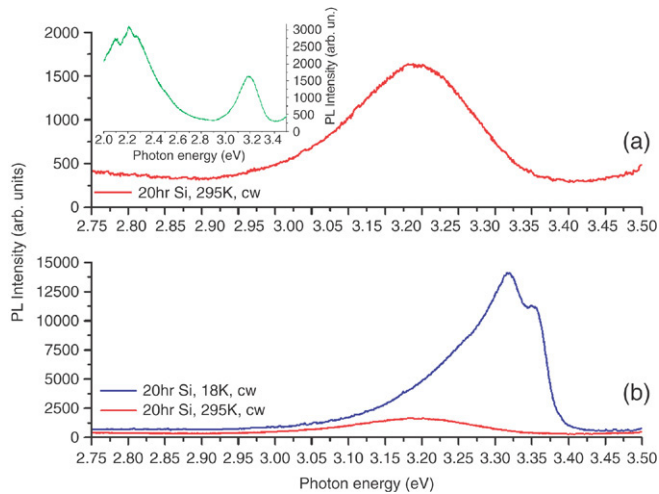
Fig. 3. PL spectra of ZnO nanostructures grown on Si(100) for 20 h. The spectra are recorded at (a) 295 K and (b) 18 K using a 325 nm He–Cd cw laser as the excitation source. In the inset of (a) the visible range of the PL spectrum is also displayed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

substrate coverage of ∼70–80%. The flowerlike nanostructures consist of uniform nanorods with a typical diameter of around 700–800 nm and length of several microns (∼10–12 μm). All nanorods have hexagonal cross section (see inset of Fig. 2(b)), implying the occurrence of the wurtzite hexagonal ZnO crystal structure as demonstrated by XRD. Fig. 2(c) and (d) show SEM micrographs of ZnO nanostructures grown on Si(100) substrates for 1 h and 5 h, respectively. Flowerlike nanostructures can be generally observed for both growth periods. With increasing time, though, the nanostructures become gradually larger. For 1 h growth the nanorods' diameter is ∼500 nm and their length varies from 5–8 μm, while after 5 h growth there are quite a lot of larger flowerlike nanostructures consisting of nanorods with a typical diameter of 700–800 nm and length of ∼ 8 μm (Fig. 2(c) and (d)). However, the small flowerlike nanostructures which are dominant for 1 h growth are still present, but at a quite smaller fraction. The coverage of the substrate area was estimated at ∼35% for 1 h and ∼60% for 5 h growth. It should be also noted that the substrate coverage increases for Si(100) compared with glass.

Photoluminescence (PL) spectra of the ZnO nanostructures were obtained at RT in the wavelength range from 350 to 650 nm using a He–Cd cw laser (325 nm) as the excitation source. Fig. 3(a) displays the characteristic PL spectrum at RT of a ZnO sample deposited on Si(100) for 20 h. The PL spectrum contains a broad UV emission band centered at ∼3.192 eV as well as a wide green to red band (see the inset of Fig. 3(a)). The UV emission is originated from excitonic recombination corresponding to the near band-gap emission of ZnO, while the emission bands in the visible range are due to the recombination of photo-generated holes with singly ionized charge states in intrinsic defects such as oxygen vacancies, Zn interstitials, or impurities [1,2,15,16].

We shall next focus on the UV emission band of the ZnO nanostructures deposited by the ACG method. The PL spectrum at RT of the 20 h ZnO sample on Si(100) exhibits only a relatively broad UV emission band centered at ∼3.192 eV (Fig. 3(a)). At 18 K, we recognize two luminescence bands at 3.319 and 3.356 eV. These bands could be attributed to the radiative recombination of bound and free excitons respectively [1,15]. Finally, in Fig. 4, the effect of
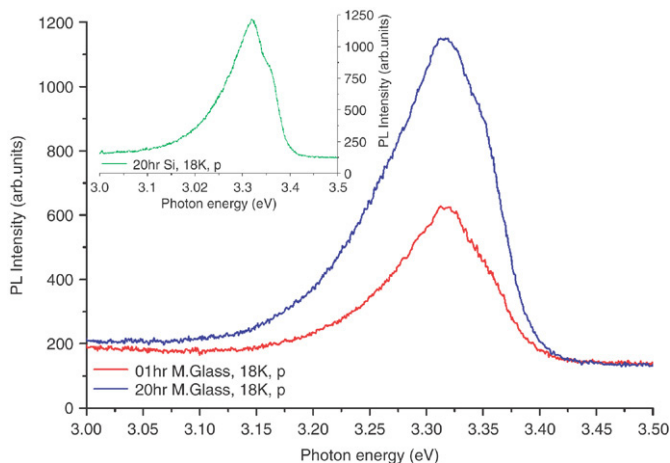
Fig. 4. PL spectra at 18 K of ZnO nanostructures grown on glass for 1 and 20 h. The spectra are recorded using a 266 nm pulsed laser as the excitation source. In the inset the PL spectrum of ZnO deposited on Si(100) for 20 h is also displayed.

growth time on the PL spectra, at 18 K, is elucidated for ZnO flowerlike nanostructures grown on glass (1, 20 h) excited with the 266 nm pulsed laser. The longer the growth time, the stronger the UV emission band, whereas the peak remains centered at 3.319 eV. The increase observed in the PL intensity with growth time is attributed to the better crystalline quality of the samples grown at longer deposition times, as well as the higher substrate coverage achieved.

4. Conclusions

ZnO nanostructures were successfully deposited on Si(100) and glass substrates by aqueous chemical growth. For short deposition periods sponge-like structures are formed which with increasing growth time transform into flowerlike architectures consisting of uniform nanorods pointing to different directions. The geometrical characteristics of the rods depend among other parameters on the growth time. All nanostructures synthesized possess the wurtzite hexagonal crystal structure of ZnO and show very good crystalline quality. The photoluminescence spectra of the flowerlike ZnO nanostructures exhibit a strong UV excitonic peak at low temperatures (18 K) that persists up to room temperature.

Acknowledgements

References

[1] U. Ozgur, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, H. Morkoc, J. Appl. Phys. 98 (2005) 041301.
[2] D.C. Look, Mater. Sci. Eng. B 80 (2001) 383.
[3] B.P. Zhang, N.T. Bihn, Y. Segawa, Y. Kashiwaba, K. Haga, Appl. Phys. Lett. 84 (2004) 586.
[4] H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, Adv. Mater. 13 (2001) 113.
[5] H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, N. Tran, E. Weber, R. Ruso, P. Yang, Science 292 (2001) 1897.

[6] J.H. Choi, H. Tabata, T. Kawai, J. Cryst. Growth 226 (2001) 493.
[7] C. Liu, J.A. Zapien, Y. Yao, X. Meng, C.S. Lee, S. Fan, Y. Lifshitz, S.T. Lee, Adv. Mater. 15 (2003) 838.
[8] S.C. Lyu, Y. Zhang, H. Ruh, H.J. Lee, H.W. Shim, E.K. Suh, C.J. Lee, Chem. Phys. Lett. 363 (2002) 134.
[9] B.D. Yao, Y.F. Chen, N. Wang, Appl. Phys. Lett. 81 (2002) 757.
[10] J.J. Wu, S.C. Liu, J. Phys. Chem. B 106 (2002) 9546.
[11] X.T. Zhang, Y.C. Liu, L.G. Zhang, J.Y. Zhang, Y.M. Lu, D.Z. Shen, W. Xu, G.Z. Zhong, X.W. Fan, X.G. Kong,
     J. Appl. Phys. 92 (2002) 3292.
[12] S.W. Kim, Sz. Fujita, Sg. Fujita, Appl. Phys. Lett. 81 (2003) 5036.
[13] L. Vayssieres, Adv. Mater. 15 (2003) 464.
[14] Q. Li, V. Kumar, Y. Li, H. Zhang, T.J. Marks, R.P.H. Chang, Chem. Mater. 17 (2005) 1001.
[15] T.W. Kim, T. Kazawoe, S. Yamazaki, M. Ohtsu, T. Sekiguchi, Appl. Phys. Lett. 84 (2004) 3358.
[16] Z. Qiu, K.S. Wong, Appl. Phys. Lett. 84 (2004) 2739.