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Synthesis and enhancement of ultraviolet emission by post-thermal treatment of unique zinc oxide comb-shaped dendritic nanostructures

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Abstract

ZnO comb-shaped dendrites are synthesized by a vapor transport method. Systematic scanning electron microscopy studies of unique nanocomb-shaped dendrites after periodic heat treatments gives direct evidence of sublimation. The ultraviolet (UV) and visible emission depends strongly on the annealing temperatures and the luminescent efficiency of UV emission is enhanced significantly with each subsequent heat treatment.

Keywords: Nanostructure (ZnO); Nanocombs; Optical Properties

1. Introduction

The study of different ZnO nanostructures has attracted much research attention because of their excellent optical, electrical, gas sensing and piezoelectric properties [1–4]. Hierarchical assembly of nanoscale building blocks (nanocrystals, nanowires, and nanotubes) is a crucial step towards realization of functional nanosystems and represents a significant challenge in the field of nanoscale science [5]. Self-organized hierarchical nanostructures grown from a number of materials have generated much attention [6]. A good example of such nanostructures, the ZnO comb-shaped nanostructure, has been reported recently. Detailed structural analysis of this novel nanostructure suggested that self-organization of comb structures made of ordered arrays of ZnO nanowires are monolithically single crystalline [7].

Lao et al. reported pure and Sn-doped ZnO comb-shape structures [8]. Leung et al. fabricated ZnO ribbon/comb structures by simply heating ZnO: single-walled nanotube mixture in a tube furnace in air at atmospheric pressure. The ribbon/comb structures formed on the substrate in the temperature range of 750–800 °C, and their morphology was affected by both the source temperature and the choice of substrate [9]. Pan et al. [10] reported that by simply increasing the growth time, the dimensions of the single crystalline combs and even the shape of the associated nanowires can be controlled. The size of these nanostructures can be controlled by varying the Ar flow rate [11]. Recently, ZnO comb-like dendrites have been fabricated in bulk quantities by adopting a low temperature vapor process, using Zn as the starting material [12].

The formation mechanism of comb-shaped dendrites have been reported by a number of researchers. Park et al. reported that at first, one-dimensional nanowires are grown and as the reaction time increases, dendritic side branch nanowires begin to grow along the basal nanowires, resulting in highly defined and aligned comb-like architectures [13]. They have further suggested that the dendrites

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can be developed by morphological instability via a vapor–solid growth mechanism without a catalyst. So, the comb-like side branching from the nanowire appears to be related to the morphological instability in a supersaturated vapor environment [14,15]. Wang et al. suggested that the formation of nanotips and nanofinger arrays on the two sides of the comb ribbon is a direct result of the surface polarity of ZnO. The polarity of the ZnO (0001) surface plays an important role in determining the nanostructures grown on the surface. The self-catalyzed process is a likely mechanism for the growth of oxide nanostructures without the presence of foreign metallic catalysts [16].

Potential applications of hierarchical nanostructures include nanoelectronics, opto-electronics, nanocomposites, and catalysts [8]. Conductive properties of dendritic ZnO nanostructures were measured by an atomic force microscope with an Au-coated conducting tip [12]. Pan et al. [10] reported that these comb-shaped structures can also exhibit a strong diffraction effect and function as excellent microscale beam dividers. Yu et al. [17] measured photoluminescence (PL) properties, revealing a strong peak in the visible range and a relatively low intensity UV peak. Another research group reported a strong UV peak, with weak green emission, [9]. For the ZnO comb-shaped nanostructures reported recently, most researchers have focused on the morphological and structural characterization of these novel comb-shaped dendrites [7,8,14–16,18]. However, a systematic study on the effect of heat treatment on different parameters is still required and has significance for potential applications.

In this report, we demonstrate, for the first time, the systematic change in optical properties with post synthesis heat treatment of the unique ZnO comb-shaped dendrites. Direct evidence of sublimation, at temperatures much lower than the synthesis temperatures, is provided and possible reasons for the improvement in optical and structural properties are discussed.

2. Experimental procedure

Synthesis of ZnO nanostructures was based on the thermal evaporation method. Equal amounts (by weight) of ZnO powder (99.0%, Hayashi Pure Chemical Industries, Osaka, Japan) and carbon black were mixed and transferred to an alumina boat. The boat was placed in the centre of the tube furnace. Au-coated Si substrates were placed on top of an alumina boat. The experimental set-up is shown in Fig. 1(a). For the synthesis, the furnace temperature was 925 °C and the holding time 15 min. Ar was used as the carrier gas and the flow rates of Ar and O_2 were 150 and 2 sccm, respectively. The white substrate surface indicates the deposition of ZnO. Comb-shaped dendrites were transferred on Si substrate coated with thin layer of SiO_2. The substrate was heat treated in an O_2 (99.999% pure, flow rate = 25 sccm) environment in the tube furnace at different temperatures and X-ray diffraction (XRD) patterns and PL were measured after every heat treatment.

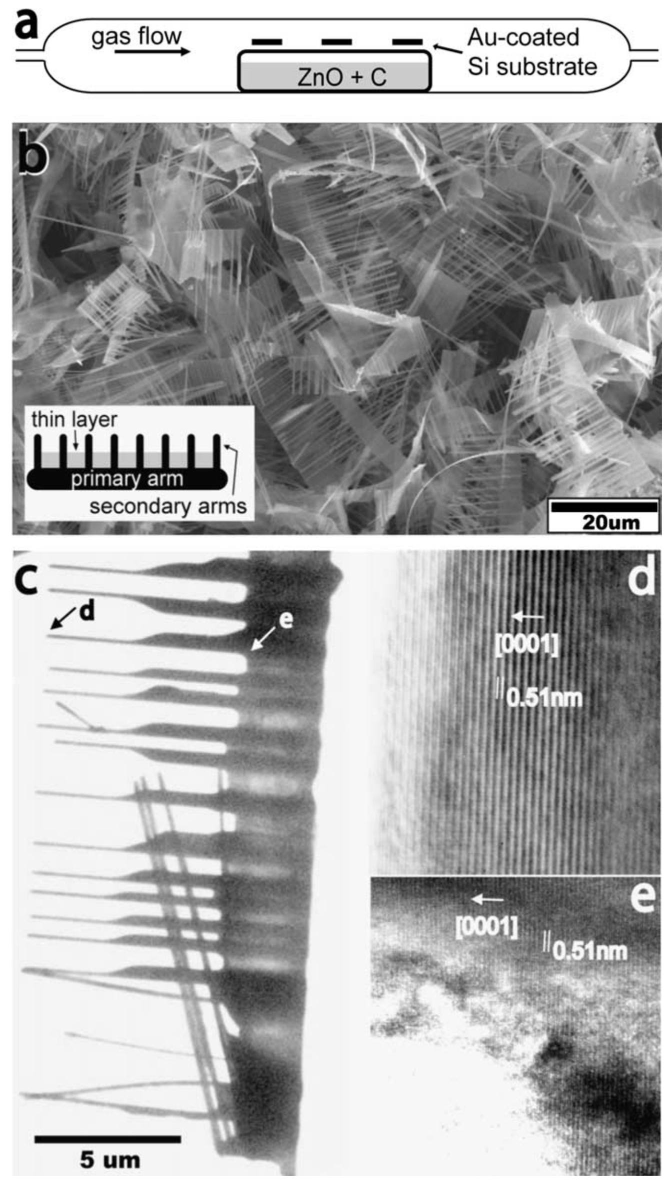

Fig. 1. (a) Schematic diagram of the experimental set-up. (b) SEM micrograph of ZnO comb-shaped dendrites deposited on Si substrate. Substrate and source were at 925 °C. (c) TEM micrograph of a representative comb-shaped dendrite suggesting no clear primary stem. (d) and (e) High resolution TEM image (HRTEM) images of different regions of the comb-shaped dendrite. The spacing of 0.51 nm between adjacent lattice planes corresponds to (0002) crystal planes.

Phase analysis of the deposited nanostructures was conducted by using the XRD (Rigaku Tokyo, Japan). At least 20 particles were averaged for the particle size measurement using scanning electron microscopy (SEM) micrographs. Room-temperature photoluminescence of the nanostructures was measured using an Xe lamp with the excited wavelength of 325 nm.

3. Results and discussion

The as-synthesized ZnO nanostructures were first examined by SEM. Fig. 1(b) shows typical images of as-synthesized ZnO comb-shaped dendrites deposited on Au-coated Si substrates. The general morphology of the samples consists of one-sided comb-shape structures. Most of the secondary arms of these comb-shaped dendrites are parallel to one another and their length may vary slightly from arm to arm. These secondary arms connect from one side to nanorod/sheet to form the comb-shaped structure. Close examination of these combs suggests that most of the nanocombs do not have a clear primary arm (main stem) and it seems that the secondary arms are placed parallel to each other and a thin layer is formed on only one side of the rods, giving it a comb-shape morphology. The inset in Fig. 1(b) shows a schematic diagram of the synthesized nanocombs. The lengths of these ZnO nanostructures were from a few 10 s to 100 s of micrometers.

Fig. 1(c) shows a typical transmission electron microscopy (TEM) image of representative ZnO comb-shaped dendrites. The dendrites are fragile and may break during TEM sample preparation. TEM micrograph further strengthens the SEM observation that the nanocombs do not have a clear primary stem. The secondary arms of these dendrites have a smooth surface, thicker from the end joined with the sheet-shape stem and thin from the free end. Structural characterization of the nanocombs was performed in high resolution mode. Fig. 1(d) shows the tip of a secondary arm and the lattice spacing of 0.51 nm between adjacent lattice planes corresponds to the distance between two (0001) crystal planes, confirming [0001] as the preferred growth direction for secondary arms. HRTEM of the area, where the secondary arm is joined with the primary stem (Fig. 1(e)) suggested that nanocombs have a single crystalline nature.

The comb-shaped structure reported in the present study is unique in the sense that most of the nanocombs do not have a clear primary arm (main stem) and it is suggested that the secondary arms are placed parallel to each other and a thin layer is formed on only one side between the secondary arms, giving it the comb-shape morphology. It is believed that a thin wire formed first, thicker secondary arms grow from the primary stem and because of the high substrate temperature (substrate and the source are at 925 °C) the primary arms re-evaporate forming a thin layer between the secondary arms. More experimental and theoretical work is needed to know the exact growth mechanism of these remarkable comb-shaped dendrites.

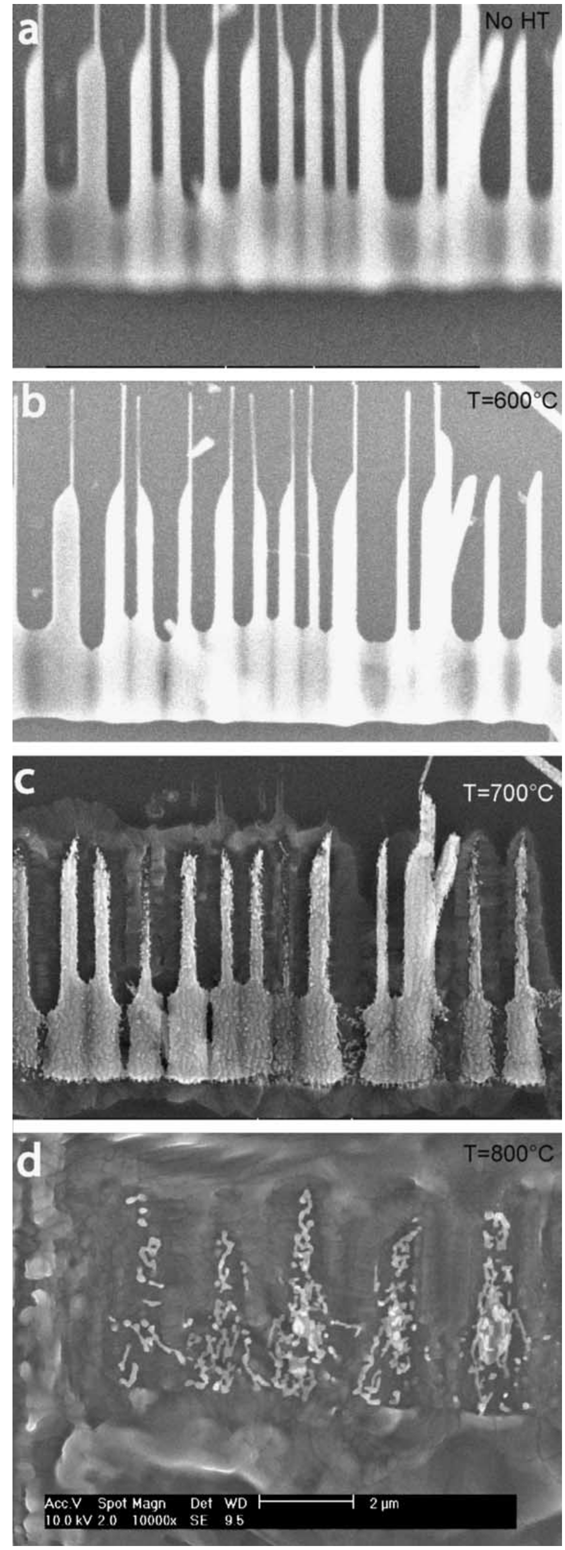

Fig. 2. SEM micrographs of nanocomb-shaped dendrites taken after every subsequent heat treatment in pure oxygen environment: (a) without heat treatment, (b) after heat treatment at 600 °C, (c) after heat treatment at 700 °C and (d) after heat treatment at 800 °C. SEM micrographs suggest significant sublimation after 700 °C.

Post-thermal annealing of ZnO nanostructures is conducted in a pure oxygen environment. A small part of the deposited powder was transferred to a Si substrate and SEM and PL properties were investigated after each heat treatment at 500, 600, 700 and 800 °C for 1 h. Fig. 2(a)–(d) shows SEM micrographs of ZnO comb-shaped structures before and after thermal annealing at 600, 700 and 800 °C. SEM micrographs clearly suggest a systematic degradation with temperature, showing no significant difference after heating at 600 °C and gradual degradation beginning at 700 °C. The surface appears to be rough, the thin film between secondary arms disappeared and the length and width of most of the secondary arms are reduced. However, the general comb-shaped structure still persists after annealing at 700 °C. When the same sample was heated to 800 °C, the comb-shaped structure disappeared and only small particles are visible in the micrograph.

Zinc oxide sublimes congruently by decomposition to the gaseous elements according to the following reaction

$$ZnO(s) = Zn(g) + 0.5O_2(g) \quad (1)$$

As the annealing temperature is raised, the sublimation rate increases. During high temperature (>600 °C) annealing, the surface morphology of bulk ZnO single crystal is affected by the evaporation of lattice constituents and the surface becomes rough due to the continuous evaporation [19,20]. As the temperature further increases (800 °C) the ZnO nanostructure is completely etched out and only nanoparticles are left. Previous reports suggested that prominent sublimation in bulk ZnO occurs at 1100 °C [21]. It is interesting to note that sublimation in nanostructures occurred at 700°C which is much lower than the synthesis temperature (925 °C). This may be because of the nanosize of the comb-shaped structure. Fig. 2 gives direct evidence that ZnO nanostructures sublimes at much lower temperatures than the synthesis temperature.

The PL spectra of ZnO comb-shaped dendrites were measured using a Xe lamp (325 nm) as the excitation source. Fig. 3 shows the room-temperature PL spectra of the ZnO comb-shaped dendrites. The spectrum of the as-synthesized ZnO dendrites mainly consists of a weak UV emission and a strong green emission. The UV emission, located at 390 nm, is the exciton recombination related near-band edge emission (NBE) of ZnO and the deep-level emission (DLE) at 530 nm usually results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [22].

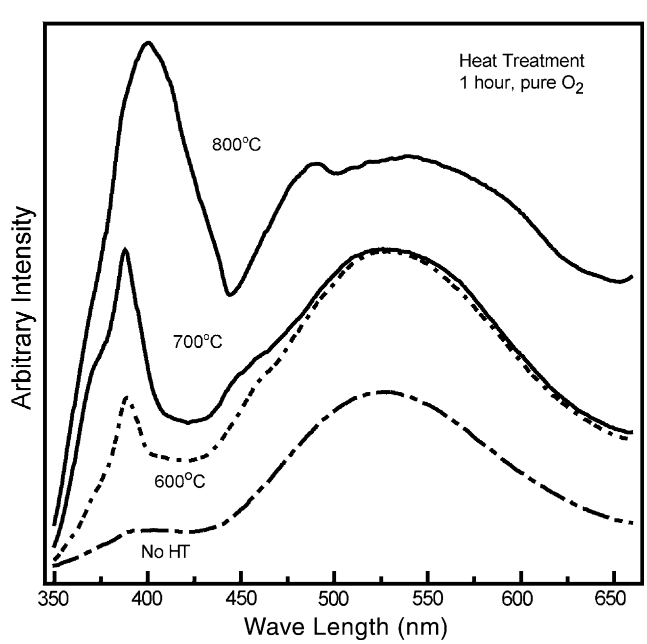

Fig. 3. Room-temperature photoluminescence spectrum of nanocombs measured using an Xe lamp (excited wavelength of 325 nm). The photoluminescence spectrum is a clear indication of the relative increase in UV intensity with respect to green intensity after every heat treatment.

The optical properties of ZnO can be tuned by annealing the samples in different environments [23]. We annealed our sample under an O_2 atmosphere at 600, 700 and 800 °C. The results suggest that the UV intensity increases gradually as the annealing temperature increases. The PL results of ZnO nanocombs clearly indicate that the UV intensity increases with increasing annealing temperature with no significant change in the DLE intensity after heat treatment at 600 °C. Previous researchers have suggested that defects may degrade the performance of optical devices fabricated from III–V semiconductors [24]. Ko et al. [25] found a correlation between UV intensity and threading dislocations present in the ZnO epilayer, suggesting that UV intensity increases with the decrease in threading dislocation concentration. Two groups independently concluded that after annealing ZnO films, the UV peak increases significantly, indicating that quality of the ZnO film was improved through annealing [26,27]. Therefore it can be deduced that post synthesis heat treatment plays an important role in tuning the PL properties and the increase in the UV intensity is possibly because of the improvement in the crystal quality of the ZnO comb-shaped nanostructures after annealing at different temperatures.

Fig. 3 also suggests that the intensity of the DLE increase with the increase in the heat treatment temperatures. However, the increase is relatively less than the UV peak. Point defects, i.e. oxygen vacancies, oxygen interstitials, zinc vacancies, and impurities are considered to be possible origins for these bands [22,28]. The increase of DLE with annealing time suggests that the DLE related defects cannot be removed by annealing and, on the contrary, the annealing conditions actually favor their formation. Point defects at compound semiconductor surfaces are, for entropy reasons, thermodynamically stable at high temperatures [29]. Therefore it is difficult to remove completely the point defects in ZnO nanostructures by thermal treatment only and a minor peak may always be present in the PL data.

The evolution of the XRD results with different annealing temperatures is shown in Fig. 4. XRD results suggest that only ZnO peaks are present, and no peaks of Zn or other phases appear in any of the samples. Also, no preferred orientation, i.e. (0002) growth can be seen before or after the thermal treatment of nanocombs. The XRD (101) peak related to the ZnO comb-shaped dendrites has full width at half-maximum (FWHM) for the annealed ZnO comb-shaped structures narrower than that for the as grown samples. The angular peak position of bulk crystalline ZnO with (101) orientation is $2\theta = 36.255°$ (JCPDS card # 65-3411). The XRD (101) peak for ZnO comb-shaped dendrites is at a lower angle for as-synthesized combs. When heated at 600 °C the peak shifts towards a higher angle which is much closer to the above-mentioned

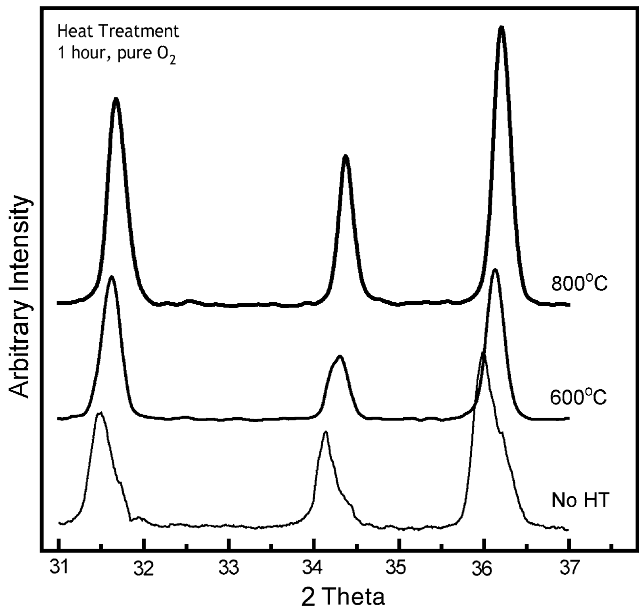

Fig. 4. XRD results for ZnO dendrites before and after heat treatment at 600 and 800 °C. The continuous shift in the peak towards a higher angle and narrower FWHM after every heat treatment suggests better crystallinity.

JCPDS card # 34-3414. The peak shift and narrow FWHM may be due to high annealing temperatures which help to enhance the mobility of atoms, subsequently resulting in reduced defect concentration and improving the quality of ZnO crystal [30,31].

The PL data and XRD results support each other. The increase in UV and XRD intensities suggests a decrease in the crystal defects and an improvement in the quality of ZnO. The XRD peak shift towards a higher angle also indicates an improvement in the overall crystal structure. Hence it can be suggested that high annealing temperatures provide energy to ZnO atoms to enhance mobility and diffusion which could decrease the defects and improve the quality of the ZnO comb-shaped structures [30].

4. Conclusion

ZnO comb-shaped dendrites were synthesized by a vapor transport method. The unique comb-shaped dendrites are single crystalline in nature with no prominent primary stem and only thin film is present between the secondary arms. Heat treatment has been proven to tune the photoluminescence properties of ZnO nanostructures. A consistent increase in the UV peak relative to the green emission with the increase in post annealing temperature suggests that the luminescent properties could be controlled by heat treatment. XRD and PL results support each other, indicating that crystal quality gradually improved with each subsequent heat treatment, which may be attributed to the higher mobility resulting in reduced defect concentration.

References

[1] Law M, Goldberger J, Yang P. Annu Rev Mater Res 2004;34:83–122.
[2] Kolmakov A, Moskovits M. Annu Rev Mater Res 2004;151.
[3] Chen Z, Wu N, Shan Z, Zhao M, Li S, Jiang CB, et al. Scripta Mater 2005;52:63.
[4] Xu C, Liu Z, Liu S, Wang G. Scripta Mater 2003;48:1367.
[5] Wu YY, Yan H, Huang M, Messer B, Song J, Yang PD. Chemistry, Eur J 2002;8:1260.
[6] Yong-Qin C, Da-Peng Y, Guo-Hua L, Zai-Li F, Ye Z, Yao-Feng C, et al. Chin Phys Lett 2004;21:2301.
[7] Yan H, He R, Johnson J, Law M, Saykally RJ, Yang P. J Am Chem Soc 2003;125:4728.
[8] Lao JY, Huang JY, Wang DZ, Ren ZF. J Mater Chem 2004;14:770.
[9] Leung YH, Djuris'ic' AB, Gao J, Xie MH, Wei ZF, Xu SJ, et al. Chem Phys Lett 2004;394:452–7.
[10] Pan ZW, Mahurin SM, Dai S, Lowndes DH. Nano Lett 2005;5:723.
[11] Manzoor U, Kim DK, J Cryst Growth, submitted for publication.
[12] Zhi-Min L, Hong-Zhou Z, Jun X, Da-Peng Y. Chin Phys Lett 2005;22:987.
[13] Park J-H, Choi H-J, Choi Y-J, Sohn S-H, Park J-G. J Mater Chem 2004;14:35.
[14] Park J-H, Choi H-J, Choi Y-J, Sohn S-H, Park J-G. J Cryst Growth 2005;280:161.
[15] Park J-H, Choi H-J, Park J-G. J Cryst Growth 2004;263:237–42.
[16] Wang ZL, Kong XY, Zuo JM. Phys Rev Lett 2003;91:185501.
[17] Yu S-H, Yang J, Qian Y-T, Yoshimura M. Chem Phys Lett 2002;361:362–6.
[18] Ma C, Moore D, Li J, Wang ZL. Adv Mater 2003;15:228.
[19] Kohl D, Henzler M, Heiland G. Surf Sci 1974;41:403.
[20] Grunze M, Hirschwald W, Hofmann D. J Cryst Growth 1981;52:241.
[21] Iwanaga H, Yoshiie T, Yamaguchi T, Shibata N. J Cryst Growth 1979;47:703.
[22] Vanheusden K, Warren WL, Seager CH, Tallant DR, Voigt JA, Gnade BE. J Appl Phys 1996;79:7983.
[23] Lim J, Shin K, Kim HW, Lee C. Mater Sci Eng B 2004;107:301.
[24] Lin B, Fu Z, Jia Y. Appl Phys Lett 2001;79:943.
[25] Ko H-J, Yao T, Chen Y, Hong S-K. J Appl Phys 2002;92:4354.
[26] Zhang Y, Du G, Yang X, Zhao B, Ma Y, Yang T, et al. Semicond Sci Technol 2004;755:755.
[27] Wang G, Zhang G, Ketterson JB, Gatt R. Thin Solid Films 2004;460:232.
[28] Reynolds DC, Look DC, Jogai B. J Appl Phys 2001;89:6189.
[29] Gopel W. J Vac Sci Technol 1979;16:1229.
[30] Fang ZB, Yan ZJ, Tan YS, Liu XQ, Wang YY. Appl Surf Sci 2005;241:303.
[31] Kelley D, Louca D. Scripta Mater 2005;53:475.