

Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



Volume 253, No. 2, 15 November 2006 ISSN 0169-4332

applied surface science

A journal devoted to applied physics
and chemistry of surfaces and interfaces

Editors

F.H.P.M. Habraken, Utrecht, The Netherlands
H. Kobayashi, Osaka, Japan
J.E. Rowe, Raleigh, NC, USA
H. Rudolph, Utrecht, The Netherlands

Volume 253, No. 2, pp. 409–1038

15 November 2006

Available online at www.sciencedirect.com

ScienceDirect
<http://www.elsevier.com/locate/apusc>

This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>



Study of ZnO-coated SnO₂ nanostructures synthesized by a two-step process

Hyoun Woo Kim*, Seung Hyun Shim

School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

Received 21 October 2005; received in revised form 13 December 2005; accepted 13 December 2005

Available online 19 January 2006

Abstract

We investigated the influence of the ZnO coating on the properties of one-dimensional (1D) nanostructures of SnO₂. We have employed X-ray diffraction, scanning electron microscope, transmission electron microscope and photoluminescence (PL) spectroscopy to characterize both as-synthesized and ZnO-coated products. We observed that deposition process of ZnO by using an atomic layer deposition technique resulted in the SnO₂ core/ZnO shell structure. The photoluminescence of the ZnO-coated products exhibited broad bands in the UV and green region, suggesting a possible contribution of the emission from the ZnO outlayers.

© 2005 Elsevier B.V. All rights reserved.

Keywords: SnO₂; One-dimensional nanostructures; ZnO; Atomic layer deposition

1. Introduction

Since the discovery of carbon nanotubes, much technological and scientific excitement has been raised by the discovery of various forms of nanostructures [1–4]. In particular, the nanomaterials of metal-oxide-related semiconductors have been a matter of concern due to their excellent crystalline quality, chemical stability, and optical properties. Particularly, both tin oxide (SnO₂) and zinc oxide (ZnO) are important semiconductors with a wide bandgap and are regarded as the promising materials for optoelectronic devices and gas sensors [5–8].

Recently, coaxial nanocable-like one-dimensional (1D) structures comprising different kinds of materials have been successfully synthesized not only for making nanometer scale electronic devices with a variety of functions, but also for the protection of 1D structures from contamination or oxidation [9–12]. Since the three-dimensional geometry with respect to bundles of 1D structures requires high degree of the process control for achieving the conformal coating [13], it is worth developing suitable growth method under milder conditions. Atomic layer deposition (ALD) is one of adequate techniques

satisfying these requirements because of its nature of surface controlled process.

In this paper, we have performed the coating of ZnO by ALD technique on SnO₂ 1D nanostructures. We have investigated comparatively the samples before and after the ZnO coating in terms of their structural and photoluminescence (PL) characteristics. To the best of our knowledge, this is first report on the coating of ZnO layers on the SnO₂ 1D structures.

2. Experimental

First, we have prepared the 1D nanostructures of SnO₂ by using Sn powders. The Au-coated Si substrate was put on top of an alumina boat loaded with the pure Sn powders. The alumina boat was put in the middle of quartz tube inserted in a horizontal tube furnace. During the experiment, the furnace was maintained at a temperature of 900 °C under a constant total gas pressure of 1 T for 2 h. After the furnace was cooled down, the sample was removed from the furnace and then was transferred to an ALD chamber.

Subsequently, we have carried out the ZnO coating experiments on the as-grown SnO₂ samples by using the ALD technique. The schematic diagram of the deposition system is shown in Fig. 1. Diethylzinc (DEZn) and H₂O were kept in bubblers at 10 °C. These source gases were alternately fed into the chamber through separate inlet lines and nozzles.

* Corresponding author.

E-mail address: hwkim@inha.ac.kr (H.W. Kim).

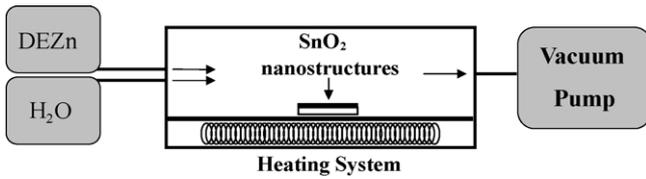


Fig. 1. Schematic diagram of the ALD system.

The typical pulse lengths were 0.2 s for DEZn, 0.2 s for the H₂O and 2 s for purging the reactants. The substrate temperature and pressure in the chamber were set to 150 °C and 0.3 T, respectively. In our previous studies of the deposition of ZnO films onto flat substrates, nucleation and growth was successfully achieved [14].

The structural properties of the product were characterized by X-ray diffraction (XRD) (Philips X'pert MRD diffractometer with Cu K α radiation), field emission scanning electron microscopy (FE-SEM) (Hitachi, S-4200), transmission electron microscopy (TEM) (Philips, CM-200), and energy dispersive X-ray spectroscopy (EDX). For TEM observation, the products were ultrasonically dispersed in acetone, and then a drop of the suspension was placed on amorphous carbon films supported by copper grids and dried in air. PL was conducted at room temperature with the 325 nm line from a He–Cd laser (Kimon, 1K, Japan).

3. Results and discussion

Fig. 2a and b, respectively, show typical top-view SEM images of the as-synthesized and ZnO-coated products, indicating that both products consist of 1D structures. Statistical analysis of many SEM images indicated that the average width or diameter of produced 1D structures was in the range of 50–1300 nm, whether the ZnO coating had been performed or not. Fig. 2c and d show the closer-view SEM images of as synthesized and ZnO-coated SnO₂ structures, respectively, indicating that the ZnO-coated product has a rougher surface than the as-synthesized one.

Fig. 3a shows a low magnification TEM image of an as-synthesized SnO₂ 1D nanostructure, indicating that the structure has a straight-line morphology. A local high resolution TEM (HRTEM) image of an as-synthesized 1D nanostructure (spot B in Fig. 3a) is shown in Fig. 3b, appearing to be structurally uniform with a clean surface. The interplanar spacings are about 0.32 and 0.34 nm, respectively, corresponding to the (0 0 1) and (1 1 0) planes of tetragonal rutile SnO₂. The associated selected area electron diffraction (SAED) pattern (in set in Fig. 3b), recorded perpendicular to the long axis, can be indexed for the $[\bar{1}10]$ zone axis of a tetragonal rutile SnO₂. Not only the TEM image but also the SAED pattern indicates that the SnO₂ structure is single crystalline.

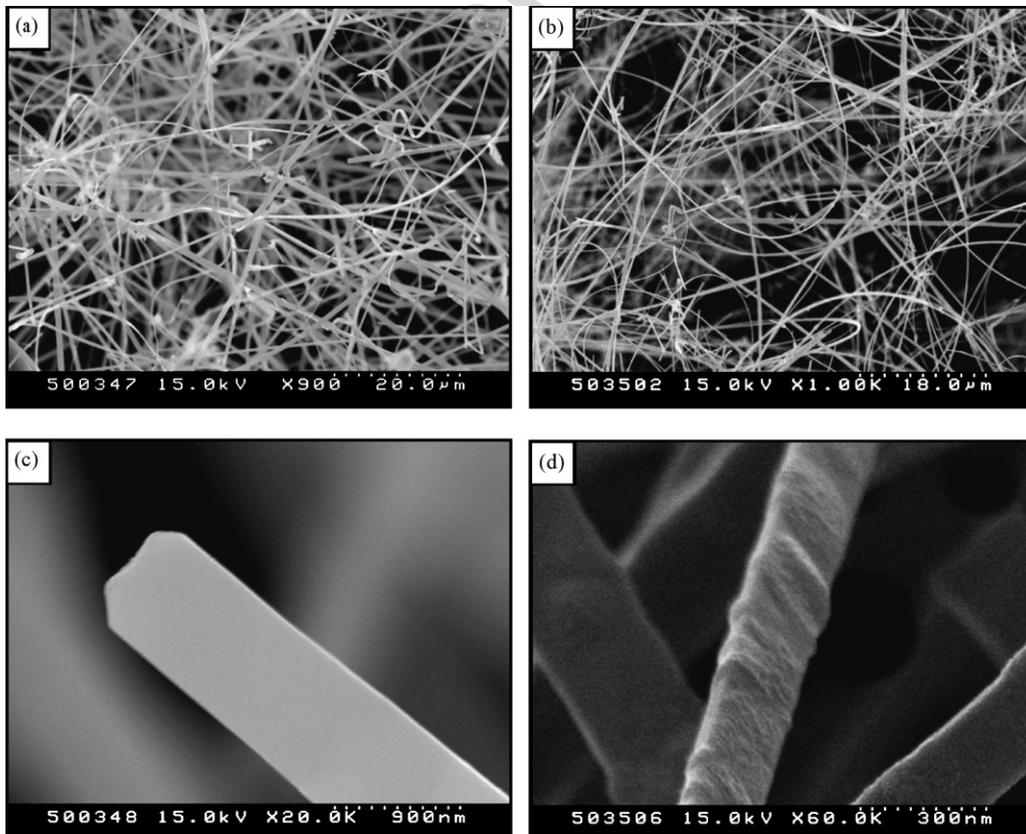


Fig. 2. Top-view SEM images of the (a) as-synthesized and (b) ZnO-coated products. High magnification SEM images of the (a) as-synthesized and (b) ZnO-coated products.

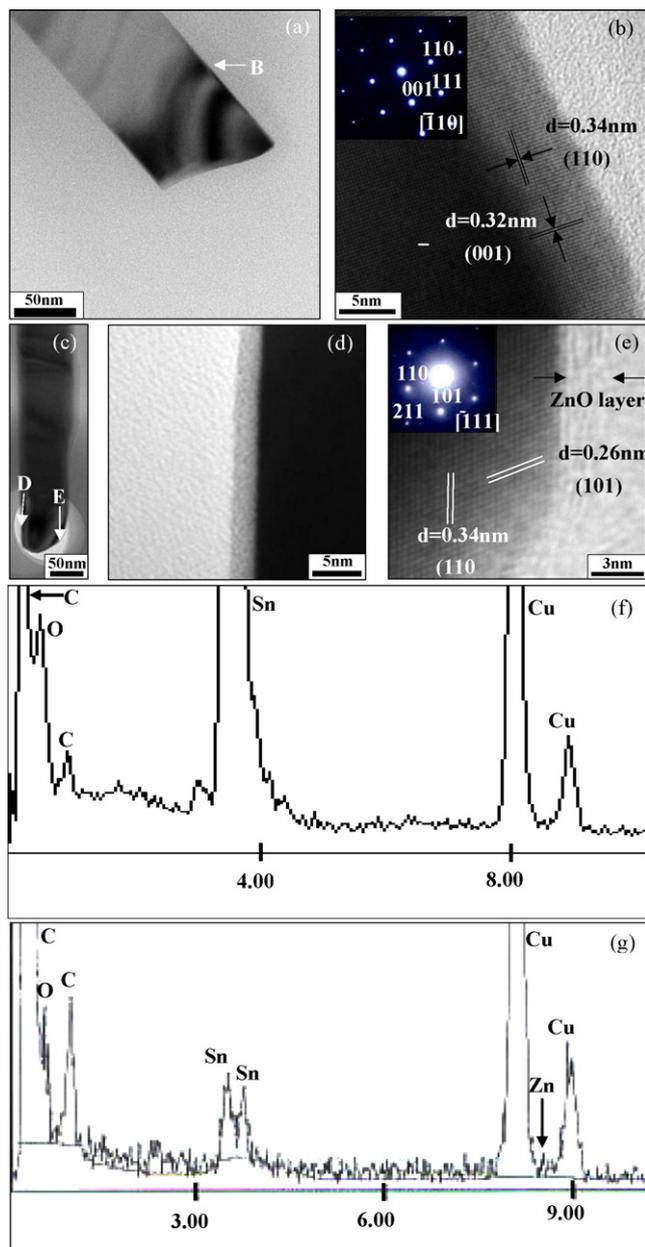


Fig. 3. (a) Low magnification TEM image of an as-synthesized structure. (b) Local HRTEM image at spot B (Inset: SAED pattern of the $[\bar{1}10]$ zone axis). (c) Low magnification TEM image of a ZnO-coated structure. (d) Local TEM image at spot D. (e) Local HRTEM image at spot E (Inset: SAED pattern of the $[\bar{1}11]$ zone axis). EDX spectrum of (f) as-synthesized and (g) ZnO-coated 1D nanostructure.

Fig. 3c shows a low magnification TEM image of an 1D nanostructure after ZnO coating, indicating that there is a layer of mist around the structure. A local TEM image (spot D in Fig. 3c) is shown in Fig. 3d, revealing that a solid layer with an average thickness of approximately 2.5 nm covers the surface of the structure. Fig. 3e shows a local HRTEM image (spot E). While the core of the coated structure is single crystalline evidenced by associated selected area electron diffraction (SAED) pattern (inset in Fig. 3e) and clearly visible lattice fringes, the shell is not single crystalline.

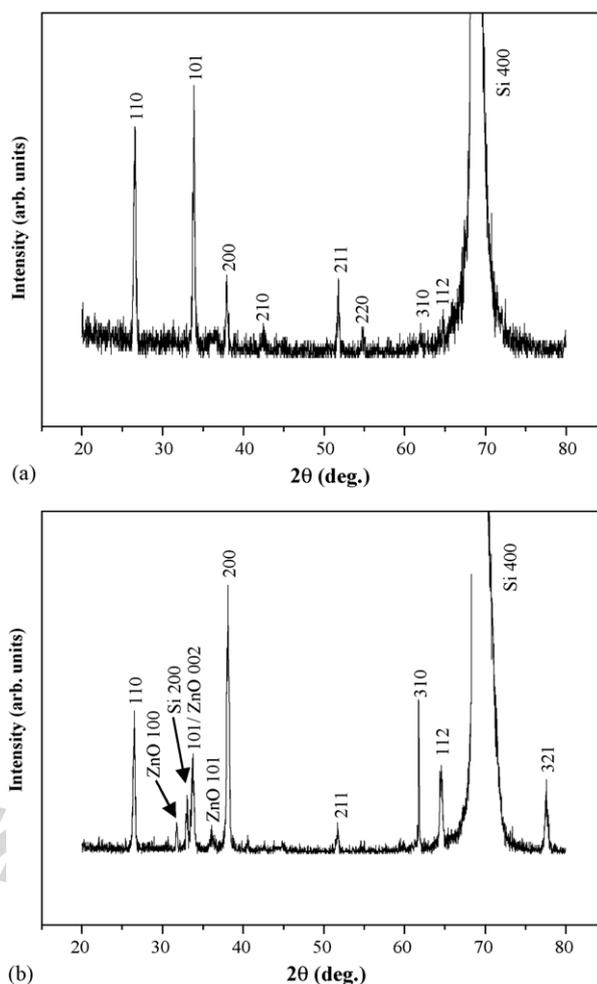


Fig. 4. XRD pattern of the (a) as-synthesized and (b) ZnO-coated products.

While the EDX pattern of the as-synthesized SnO_2 (Fig. 3f) show only elemental Sn and O (The C and Cu components have originated from the C-coated Cu TEM grid), the EDX of the coated products (Fig. 3g) shows Zn, as well as Sn and O. Moreover, since EDX spectrum made on the shell region has a relatively higher Zn/Sn atomic ratio than the similar spectrum obtained on the core region away from the shell layer (not shown here), we reveal that the outlayer comprises a Zn element. Besides, we suppose that the outlayer also comprises an O element.

Fig. 4a and b show the XRD patterns of the samples before and after ZnO coating, respectively. The Miller indices are indicated on each diffraction peak. The diffraction peaks can be readily indexed to the tetragonal rutile structure of SnO_2 with lattice constants of $a = 4.738 \text{ \AA}$ and $c = 3.187 \text{ \AA}$ (JCPDS File No. 41-1445). Some weak ZnO-related peaks are observed in the XRD spectrum from the ZnO-coated samples. It is noteworthy that although Si peaks from the substrates can be observed, no obvious reflection peaks from the impurities, such as SnO or Zn_2SnO_4 , were detected, indicating the high purity of the products.

XRD analysis confirms that ZnO crystallites may have been formed locally in the ZnO-coated samples. Therefore, the EDX

spectrum, the XRD pattern, and the observation from the previous experiments under the similar condition revealing the successful deposition of ZnO films on flat substrates, coincidentally suggest that the shell layer formed on the surface of the SnO₂ structure be ZnO. Additionally, TEM image indicates that the ZnO-coated SnO₂ may indeed have the SnO₂ core/ZnO-shell structure.

The possible growth mechanism of SnO₂ nanostructures by the present synthesis route was previously explained [15]. There are two well-accepted mechanisms for the growth of 1D nanostructures; the vapor–liquid–solid (VLS) and the vapor–solid (VS) mechanism. The VLS growth is a catalyst-assisted process, in which the metal catalyst particle acts as liquid-forming agent. In the present work, although Au-coated substrates were employed, there was no evidence that a catalyst is present at tips of the structures. Hence, the growth of the SnO₂ structure in the present route cannot be dominated by a VLS mechanism. This type of growth, which is close to a VS process, might be attributed to a diffusion-limited process in a supersaturated environment [16]. Herein, the Sn vapors generated from the Sn powders combines with oxygen, to form SnO vapors which is metastable, spontaneously decomposing into liquid Sn and solid SnO₂. The SnO₂ nuclei precipitated on the substrate grow into SnO₂ nanobelts along with incoming of air, via the VS mechanism [17]. Subsequently, for the ALD growth, DEZn and H₂O were alternately fed into the chamber with the time period of purging the reactants for depositing the ZnO outlayers on SnO₂ nanostructures. Previous studies reported the feasibility of uniform coating of 1D nanostructures by using the ALD technique [12,18].

Fig. 5a shows the PL spectra of the as-synthesized and ZnO-coated products, respectively, measured at room temperature. PL spectrum of the as-synthesized products is characterized by a broad emission band peaked at around yellow region. The yellow emission band is mainly attributed to defect levels within the band gap of SnO₂ [19,20]. We found that the shape of normalized PL spectrum was significantly changed by the ZnO coating. After multi-peak Gaussian fitting to all three major bands in the PL spectrum of the ZnO-coated products (Fig. 5b), we found that the Gaussian curves fit the original curves almost perfectly. The peak positions of the three Gaussian bands are located at about 370, 535, and 594 nm, respectively. It is noteworthy that there exists an emission band with a peak wavelength at around 594 nm (peak 1 in Fig. 5b), possibly originating from the SnO₂ core. Additionally, there is a UV emission band around the wavelength of 370 nm (peak 2 in Fig. 5b) presumably resulting from the emission mechanism associated with excitons in ZnO [21–23]. Several researchers have previously reported the UV emission from ZnO, which is not single crystalline [24–26], suggesting that the UV emission comes from the ZnO shell layer. The green emission at about 535 nm (peak 3 in Fig. 5b) may originate from ZnO core [27–29] or ZnO/SnO₂ interfaces [30], being known to be related to the defects such as oxygen vacancies [27,28]. Additionally, it is possible that the ZnO/SnO₂ heterostructures may have induced a new type of emission [30]. Although further study is necessary to reveal the detailed emission mechanism, the

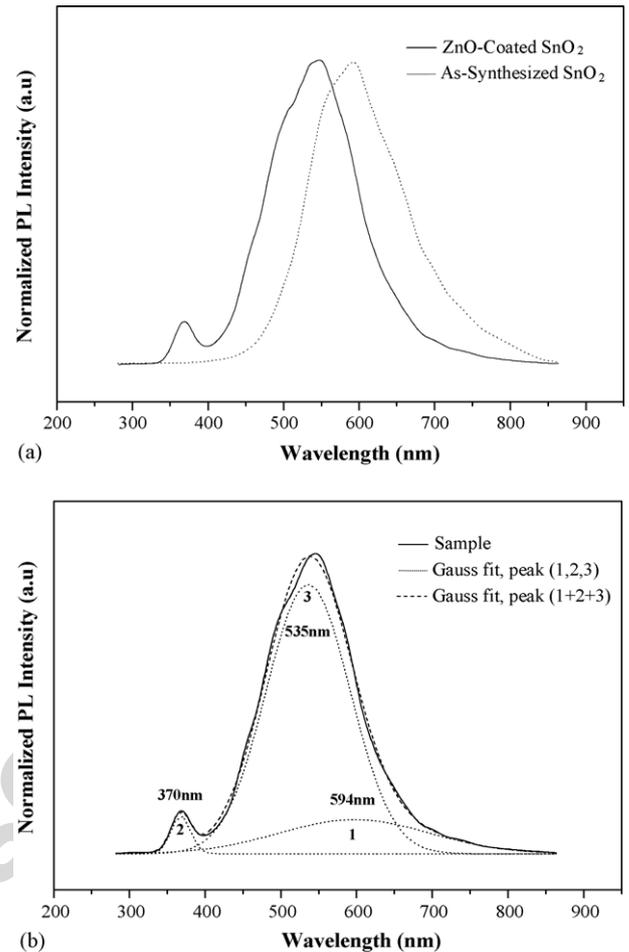


Fig. 5. (a) PL spectra of as-synthesized and ZnO-coated products. (b) PL spectrum of ZnO-coated products with the multi-peak Gaussian fitting.

appearance of UV band and a relatively strong green emission in the coated sample (compared to the uncoated ones) is due to the ZnO coating. This result will contribute to the potential applications of coaxial 1D nanostructures to optoelectronic devices.

4. Conclusions

In summary, for the first time, we have coated SnO₂ 1D nanostructures with ZnO. We have employed an ALD technique, in which DEZn and H₂O were used as precursors for zinc and oxygen, respectively. TEM and HRTEM images of ZnO-coated structure show that ZnO shell layers wrap the SnO₂ nanostructures. EDX spectra reveal that the ZnO-coated product comprises Zn element, while the uncoated one does not. XRD of ZnO-coated product indicates the existence of ZnO as well as SnO₂. The ZnO coating significantly changes the shape of normalized PL spectrum, presumably inducing UV and green emission band.

Acknowledgement

This work was supported by Korea Research Foundation Grant (KRF-2004-003-D00141).

References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] C.B. Murray, C.R. Kagan, M.G. Bawendi, *Science* 270 (1995) 1335.
- [3] J. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [4] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [5] E.R. Leite, I.T. Weber, E. Longo, J.A. Varela, *Adv. Mater.* 12 (2000) 966.
- [6] A. Aoki, H. Sasakura, *Jpn. J. Appl. Phys.* 9 (1970) 582.
- [7] D.C. Reynolds, D.C. Look, B. Jogai, H. Morkoc, *Solid State Commun.* 101 (1997) 643.
- [8] K.-S. Weissenrieder, J. Muller, *Thin Solid Films* 300 (1997) 30.
- [9] Y. Zhang, K. Suenaga, C. Colliex, S. Iijima, *Science* 281 (1998) 973.
- [10] S. Han, C. Li, Z.Q. Liu, B. Lei, D.H. Zhang, W. Jin, X.L. Liu, T. Tang, C.W. Zhou, *Nano Lett.* 4 (2004) 1241.
- [11] L.J. Lauhon, M.S. Gudiksen, D.L. Wang, C.M. Lieber, *Nature* 420 (2002) 57.
- [12] B. Min, J.S. Lee, J.W. Hwang, K.H. Keem, M.I. Kang, K. Cho, M.Y. Sung, S. Kim, M.-S. Lee, S.O. Park, J.T. Moon, *J. Cryst. Growth* 252 (2003) 565.
- [13] A.W. Ott, J.W. Klaus, J.M. Johnson, S.M. George, *Thin Solid Films* 292 (1997) 135.
- [14] J. Lim, K. Shin, H. Kim, C. Lee, *Thin Solid Films* 475 (2005) 256.
- [15] H.W. Kim, S.H. Shim, *J. Korean Phys. Soc.* 47 (2005) 516.
- [16] J. Guojian, Z. Hanrui, Z. Jiang, R. Meiling, L. Wenlan, W. Fengying, Z. Baolin, *J. Mater. Sci.* 35 (2000) 63.
- [17] S.H. Sun, G.W. Meng, Y.W. Wang, T. Gao, M.G. Zhang, Y.T. Tian, X.S. Peng, L.D. Zhang, *Appl. Phys. A* (2003) 287.
- [18] M. Kang, J.-S. Lee, S.-K. Sim, B. Min, K. Cho, H. Kim, M.-Y. Sung, S. Kim, S.A. Song, M.-S. Lee, *Thin Solid Films* 466 (2004) 265.
- [19] J.Q. Hu, X.L. Ma, N.G. Shang, Z.Y. Xie, N.B. Wong, C.S. Lee, S.T. Lee, *J. Phys. Chem. B* 106 (2002) 3823.
- [20] X.S. Peng, L.D. Zhang, G.W. Meng, Y.T. Tian, Y. Lin, B.Y. Geng, S.H. Sun, *J. Appl. Phys.* 93 (2003) 1760.
- [21] D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, T.C. Collins, W. Harsch, G. Cantwell, *Phys. Rev. B* 57 (1998) 12151.
- [22] S.W. Jung, W.I. Park, H.D. Cheong, G.-C. Yi, H.M. Jang, *Appl. Phys. Lett.* 80 (2002) 1924.
- [23] J. Lim, K. Shin, H.W. Kim, C. Lee, *Mater. Sci. Eng. B* 107 (2004) 301.
- [24] X.T. Zhang, Y.C. Liu, Z.Z. Zhi, J.Y. Zhang, Y.M. Lu, D.Z. Shen, W. Xu, X.W. Fan, X.G. Kong, *J. Lumin.* 99 (2002) 149.
- [25] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, *Appl. Phys. Lett.* 72 (1998) 3270.
- [26] Z.-J. Wang, Z.-J. Wang, L.-G. Zhang, J.-S. Yuan, S.-G. Yan, C.-Y. Wang, *Chin. Phys. Lett.* 20 (2003) 696.
- [27] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983–7990.
- [28] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, *Appl. Phys. Lett.* 78 (2001) 2285.
- [29] Y. Nakanishi, A. Miyake, H. Kominami, T. Aoki, Y. Hatanaka, G. Shimaoka, *Appl. Surf. Sci.* 142 (1999) 233–236.
- [30] Q. Kuang, Z.-Y. Jiang, Z.-X. Xie, S.-C. Lin, Z.-W. Lin, S.-Y. Xie, R.-B. Huang, L.-S. Zheng, *J. Am. Chem. Soc.* 127 (2005) 11777.