



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Journal of Crystal Growth 247 (2003) 357–362

JOURNAL OF  
**CRYSTAL  
GROWTH**

[www.elsevier.com/locate/jcrysgro](http://www.elsevier.com/locate/jcrysgro)

# Copper-catalyzed ZnO nanowires on silicon (1 0 0) grown by vapor–liquid–solid process

Seu Yi Li, Chia Ying Lee, Tseung Yuen Tseng\*

*Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC*

Accepted 17 September 2002  
Communicated by D.P. Norton

## Abstract

The ZnO nanowires were synthesized using vapor–liquid–solid (VLS) growth process on copper coated p-type Si (100) substrate. Copper catalyzed the growth of ZnO nanowires of diameters 80–150 nm and lengths of 2.5–4.0  $\mu\text{m}$ . The ZnO nanowires had hexagonal structure and exhibited  $\langle 0002 \rangle$  orientation. The photoluminescence measurements showed that the ZnO nanowires had a strong ultraviolet emission at around 381 nm and a very weak green emission around 520 nm.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 73.22.–f

*Keywords:* A1. Nanostructures; A2. Vapor–liquid–solid growth; B1. Zinc oxide nanowire; B2. Semiconducting materials; B3. Optical devices

## 1. Introduction

Large efforts are being invested to prepare structures with the nanostructured materials to achieve miniaturization in electronic and optical devices. The material, ZnO, is a wide band gap (3.37 eV) semiconductor with large exciton binding energy ( $\sim 60$  meV). It is a suitable material for applications, such as piezoelectric transducers, varistors, phosphors and surface acoustic wave (SAW) devices [1–4]. As recently demonstrated, the ZnO nanowires have potential application in

fabricating short-wavelength nano-lasers. A variety of methods have been reported to synthesize nanowires of different materials. These methods include vapor–liquid–solid (VLS) mechanism process [5,10–16], chemical vapor deposition [6], laser ablation [7–8], solution routes [9], and template-based method [10]. In the VLS mechanism, gold particles which serve as catalytic sites is deposited on the substrate. Zinc vapor is generated using carbothermal or hydrogen reduction of ZnO powder [11]. The reactant zinc vapor is absorbed by the liquid droplets at high temperature. As these droplets get supersaturated with reactant vapor, the nanowires grow by precipitation on the silicon (Si) substrate from the droplets. The nanowires growth steps terminate, when the

\*Corresponding author. Tel.: +886-3-5712121-54111; fax: +886-3-5724361.

E-mail address: [tseng@cc.nctu.edu.tw](mailto:tseng@cc.nctu.edu.tw) (T.Y. Tseng).

reactant vapor flow stops or the metal tip is completely evaporated during the reaction. The catalysts that have been used are Au [11–16], Pd [13], Ag [13], and Fe [17]. Here we report for the first time the ZnO-nanowire growth on p-type Si (100) substrates using a VLS process catalyzed by copper instead of gold. This is a new method for preparing ZnO nanowires through a rapid and cost effective thermal process. The two-step VLS growth method, used in this study reduced the liquid metal size and content efficiently to promote the growth of ZnO nanowires. Furthermore, in this process we introduce the thermal annealing steps to make ZnO nanowires approach vertically on the Si substrate. The angle from Si substrate to ZnO nanowires was about 75–85°. We have, for the first time, successfully fabricated ZnO nanowires which were oblique on Si substrate without buffer layer by VLS process using copper as catalyst.

## 2. Experiment

In our experiment, p-type Si (100) substrate was cleaned following the procedure adopted by Yang et al. [3]. A thin layer of copper was deposited on the cleaned Si (100) substrate by RF-sputtering using a copper target. The copper thin film coated on Si substrate was about 70 and 150 Å thicknesses, respectively. The copper-coated Si substrate was heated in a rapid thermal annealing (RTA) furnace at 900°C for 1 h. ZnO (99.99%, –325 mesh, Alfa Aesar) and carbon (99.99%, –325 mesh, Alfa Aesar) powders were mixed, placed in a quartz boat, and loaded to the center of a tube furnace. The annealed copper/Si substrate was placed in the same boat with mixed powder. The ZnO nanowires were grown with temperatures in the range 850–950°C under flowing high-purity Ar (99.998%) gas with the gas flow rates of 5.0–40.0 sccm. The synthesized samples had a gray-violet color. We introduced two heating schedules for the fabrication of ZnO nanowires using VLS growth process: (i) directly increasing the growth temperature from room temperature to 850–950°C, (ii) increasing the growth temperature to 800°C, keeping the temperature constant for 6 min

and then further increasing the growth temperature to 850–950°C. We used XRD (MAC Science, MXP18, Japan), FE-SEM (Hitachi S-4700I, Japan), AFM (Digital instrument, USA), XPS (VG Scientific ESCALAB-250, UK), TA (Seiko SSC 5000, Japan), TEM (Philips tecani-20, USA), and PL (Hitachi F-4500, Japan) to carry out the characterizations of crystal structure, surface morphology, chemical composition and optical properties, respectively, of the ZnO nanowires.

## 3. Results and discussion

The FE-SEM surface morphologies of ZnO nanowires are shown in Fig. 1. The tilted 45° image of Fig. 1(a) shows that the ZnO nanowires have grown uniformly at high yield. The diameters of ZnO nanowires are about 80–150 and 170–200 nm, catalyzed by 70 and 150 Å thick copper films, respectively, and their lengths are all about 2.5–4.0 μm. The thickness of copper thin film influenced the diameter of ZnO nanowires. Thicker copper films coated on the Si substrate resulted in larger diameter ZnO nanowires. Figs. 1(c) and (d) show these different diameters of ZnO nanowires formed with different thicknesses of copper thin films. The cross-section of ZnO nanowires in Fig. 1(c) shows that ZnO nanowires have grown almost vertically on Si (100) substrate. Fig. 1(b) shows that the top of ZnO nanowires with copper tips appear smooth, and that the ZnO nanowires have hexagonal structure as evidenced by XRD pattern.

Fig. 2 shows a typical XRD pattern of the ZnO nanowires. The peaks can be indexed based on the hexagonal structure of bulk ZnO (JCPDS No. 80-0074). The ZnO nanowires with different diameters have similar XRD patterns indicating that the nanowires are highly oriented in (0002) direction and less oriented in (100). The calculated lattice parameters of ZnO nanowires are  $a = b = 3.261 \text{ \AA}$  and  $c = 5.434 \text{ \AA}$ . No other peaks of copper or impurity phases are found in any of our ZnO nanowire samples.

AFM image of the copper film coated on Si substrate after the thermal annealing process is shown in Fig. 3(a). The thickness of copper film is

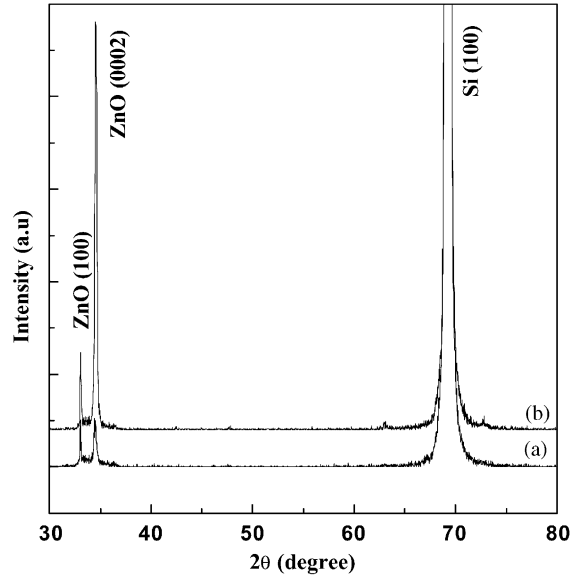
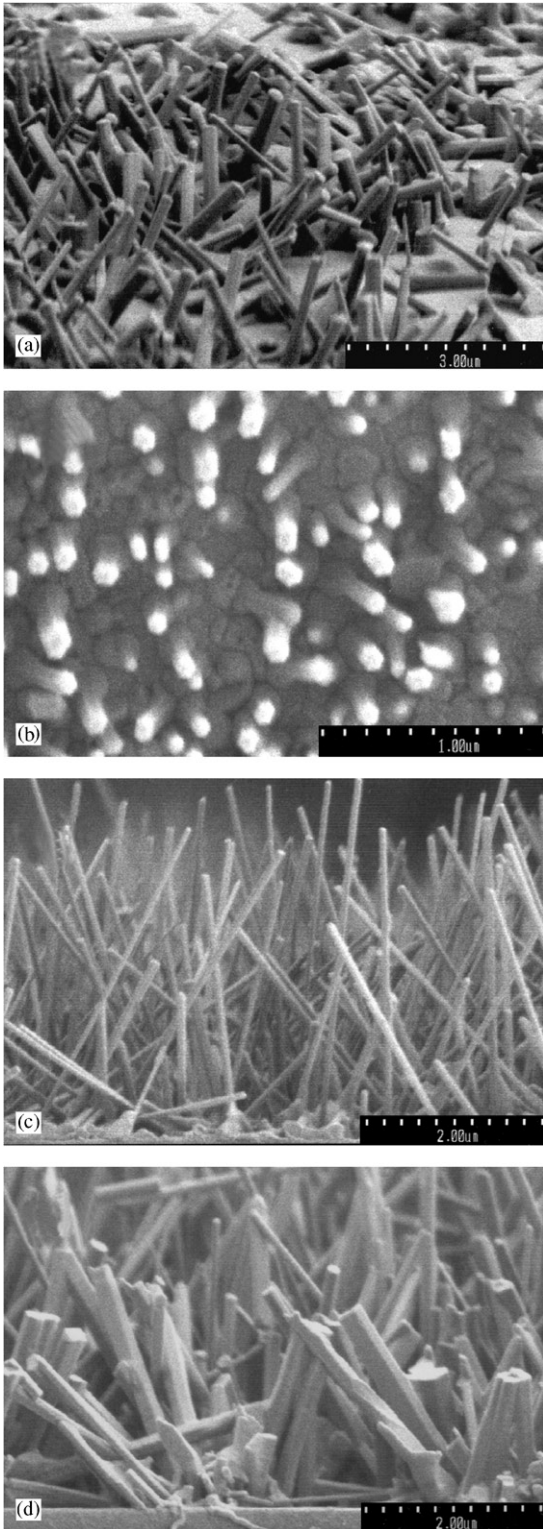


Fig. 2. XRD patterns of ZnO nanowires of diameters: (a) 170–200 nm and (b) 80–150 nm.

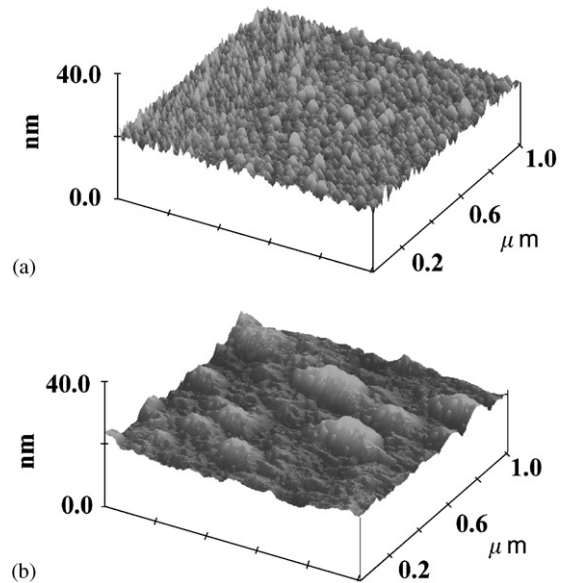


Fig. 3. AFM images of copper films after thermal annealing process: (a) 70 Å thick copper film, (b) 150 Å copper film.

←  
Fig. 1. FE-SEM images of ZnO nanowires: (a) tilt 45° view, (b) top view, (c) growth on 70 Å thickness copper film growth, (d) growth on 150 Å thickness copper film growth.

about  $70 \text{ \AA}$ . The nano-grain copper metal film forms many small solid islands, which promote self-assembled growth of ZnO nanowires. The

diameters of each of those copper islands are  $\sim 40\text{--}50 \text{ nm}$ . Absorption reaction of zinc vapor occurs in copper metal islands, when copper

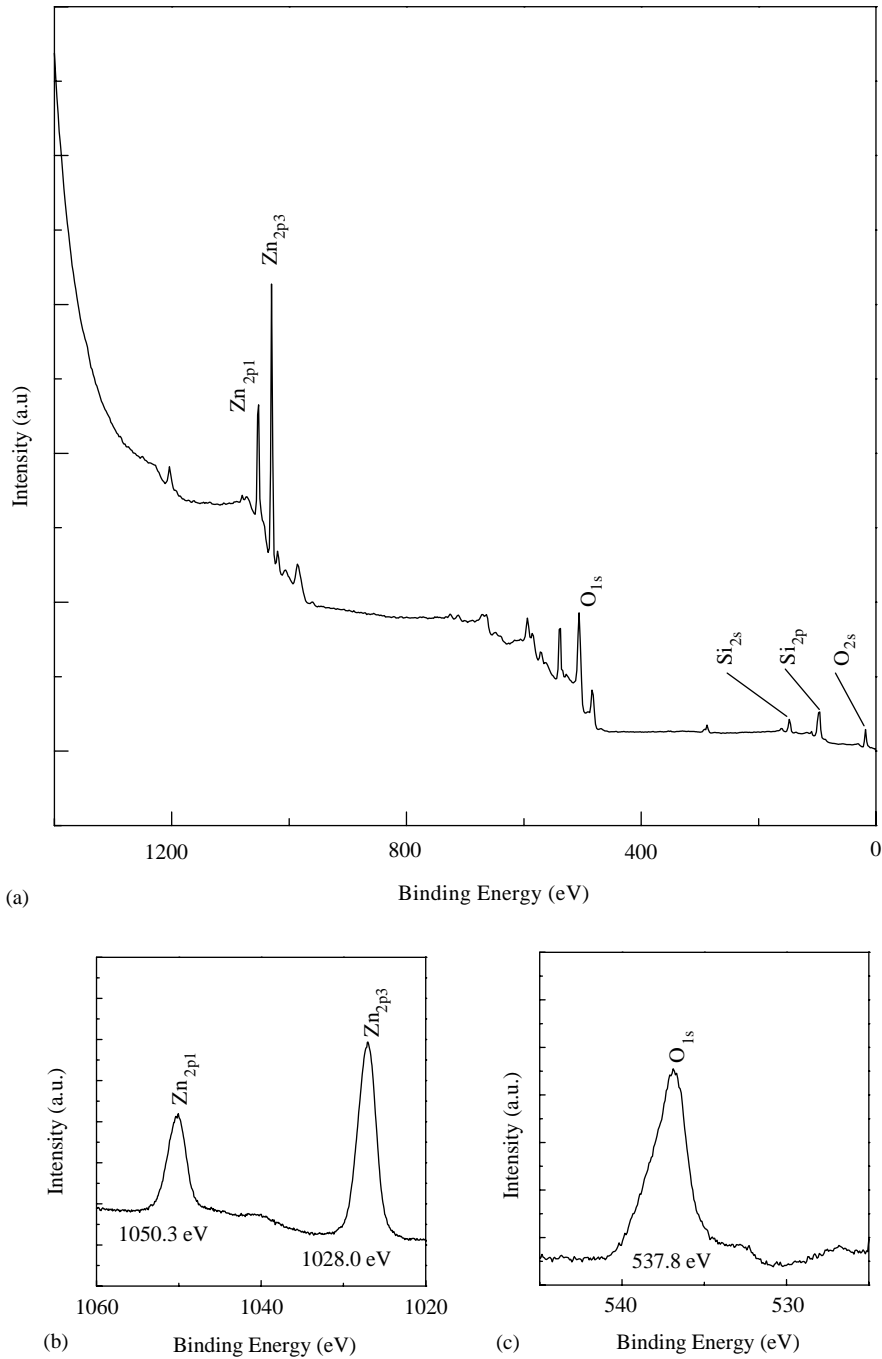


Fig. 4. XPS spectra of ZnO nanowires: (a) scanned from 0 to 1400 eV, (b) binding energy of  $\text{Zn}_{2p1}$  and  $\text{Zn}_{2p3}$ , (c) binding energy of  $\text{O}_{1s}$ .

islands are in liquid state at 900°C. The growth of ZnO nanowires ended until the supply of zinc vapor is stopped or copper tip is totally consumed. Fig. 3(b) shows the surface morphology of about 150 Å thick copper film. The diameters of copper islands are larger than 70 Å thick copper film as shown in Fig. 3(a), so the diameters of ZnO nanowires on thicker catalyst copper film are larger than thinner one. These results are consistent with the evidence from FE-SEM photographs.

The XPS analysis of the ZnO nanowires, scanned in the range of 0–1400 eV is shown in Fig. 4(a). No contaminant species are observed within the sensitivity range of the technique. The peaks at 1028.0 and 1050.3 eV are due to the binding energy of  $Zn_{2p_3}$  and  $Zn_{2p_1}$ , respectively. Peaks at 538.7 eV in Fig. 4(c) are due to  $O_{1s}$ . Because the ZnO nanowires are grown on the Si substrate, we also detect the peak corresponding to silicon. With further detailed examinations, the compositions of nanowires are consistent with stoichiometric ZnO free of other impurities such as carbon.

Fig. 5 indicates high-resolution TEM images of single-crystalline ZnO nanowires. The very clear lattice fringes between two (0002) crystal planes with d-spacing of about 2.75 Å are observed, which is in good agreement with XRD patterns at Fig. 2. Furthermore, the (10 $\bar{1}$ 1) lattice plane corresponds to the image of the side top wall of ZnO nanowires, which agrees with Laudise's [18] observation. The corresponding selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 5(a). The (10 $\bar{1}$ 0) planes of side wall of ZnO nanowires, indicate that the ZnO nanowires are single crystalline and well faceted. Fig. 5(b) shows that for samples with thicker copper films of about 150 Å, the copper tip in front of the ZnO nanowire can be very clearly seen which is an indication of a VLS process for the growth of ZnO nanowires. Fig. 5(a) also verifies that ZnO nanowires fabricated are single crystalline with no copper contamination, when the thickness of copper film is less than 70 Å.

Fig. 6 is the PL spectrum recorded on a fluorescence spectrophotometer using a Xe lamp with an excitation wavelength of 325 nm at room temperature of the ZnO nanowires. The diameters

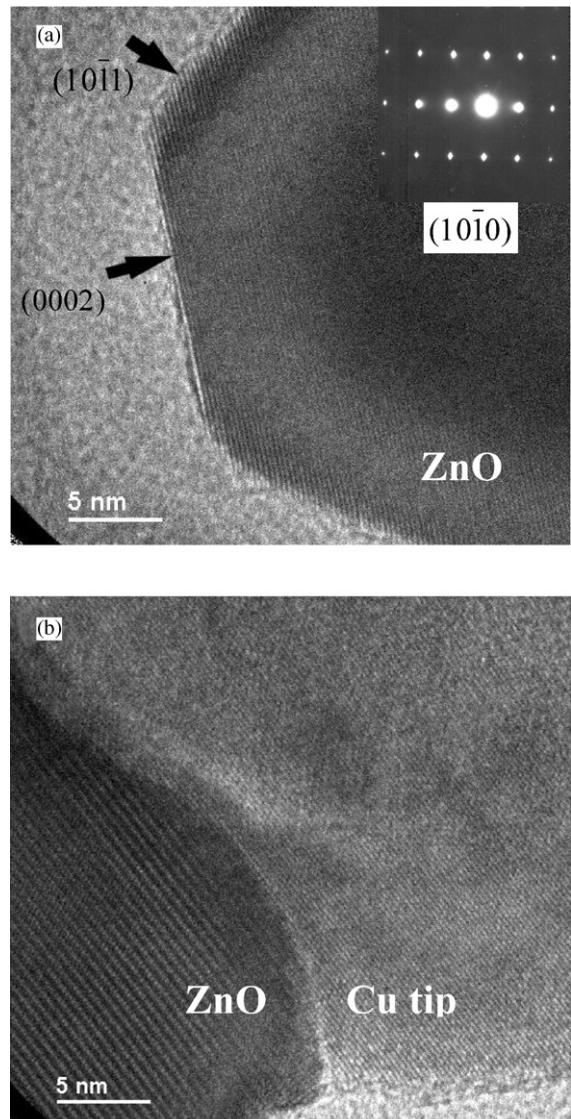


Fig. 5. TEM image of a single crystalline ZnO nanowire showing the lattice fringes. The SAED patterns (inset) along (10 $\bar{1}$ 0) direction.

of the nanowires are in the range 80–150 nm. The mean emitting bands, a strong ultraviolet (UV) emission at around 381 nm, and a very weak green emission at around 520 nm are observed. The strong UV emission is due to the near band edge emission of the wide band gap ZnO. It is reported that the high intensity of green emission can be ascribed to the high concentration of more singly

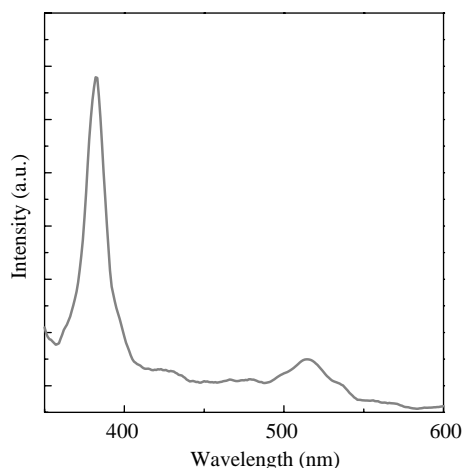


Fig. 6. Emission spectrum of ZnO nanowires using 325 nm incident Xe lamp at room temperature.

ionized oxygen vacancies in ZnO [19]. It is therefore suggested that in our epitaxial ZnO nanowires, there is low concentration of oxygen vacancies.

#### 4. Conclusions

Single crystalline (0002)-oriented ZnO nanowires are grown for the first time by copper-catalyzed VLS growth process on p-type Si(100) substrate. The diameters of ZnO nanowires within 80–150 nm are controlled by the thickness of the copper thin film. Besides, the ZnO nanowires are almost vertically grown on Si substrates by turning the thermal treatment contribution. The XRD and XPS studies determine that the composition of ZnO nanowires is stoichiometric and their structures are hexagonal. Room temperature PL spectrum of the nanowires shows a strong near band-edge UV emission at 381 nm and a weak and broad deep-level green light emission at 520 nm. We believe that the ZnO nanowires grown by the method discussed in this study could be used as semiconducting or optical light-emitting devices in nano-scale electronics and electro-optical applications at much lower production costs.

#### Acknowledgements

The authors thank Prof. M.S. Ho for valuable discussions. The measurement support of this work by the Institute of Physics, Academia Sinica, Republic of China and National Instrument Measurement Center of NTU, NCTU, NTHU are acknowledged. This work was supported by the National Science Council of ROC under contract number NSC 90-2212-E009-029.

#### References

- [1] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, *Appl. Phys. Lett.* 70 (1997) 2230.
- [2] M.T. Björk, B.J. Ohlsson, T. Sass, A.I. Persson, C. Thelander, M.H. Magnusson, K. Deppert, L.R. Wallenberg, L. Samuelson, *Appl. Phys. Lett.* 80 (2002) 1058.
- [3] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [4] Y.S. Lee, T.Y. Tseng, *J. Mater. Sci. Mater. Electron.* 9 (1998) 65.
- [5] R. Könenkamp, K. Boedecker, M.C. Lux-Steiner, M. Poschenrieder, F. Zenia, C. Levy-Clement, S. Wagner, *Appl. Phys. Lett.* 77 (2000) 2575.
- [6] M. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [7] Z.G. Bai, D.P. Yu, H.Z. Zhang, Y. Ding, X.Z. Gai, Q.L. Hang, G.C. Hiong, S.Q. Feng, *Chem. Phys. Lett.* 303 (1999) 311.
- [8] Y. Wu, R. Fan, P. Yang, *NanoLetters* 2 (2002) 83.
- [9] M.S. Gudiksen, Jianfang Wang, C.M. Lieber, *J. Phys. Chem. B* 105 (2001) 4062.
- [10] L.D. Zhsng, *Solid State Commun.* 115 (2000) 253.
- [11] X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, Y. Qian, *Chem. Mater.* 13 (2001) 1213.
- [12] J.Q. Hu, N.B. Wong Quan Li, C.S. Lee, S.T. Lee, *Chem. Mater.* 14 (2002) 1216.
- [13] R.S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* 4 (1964) 89.
- [14] M.S. Gudiksen, L.J. Lauhon, J. Fang, D.C. Smith, C.M. Lieber, *Nature* 415 (2002) 617.
- [15] Y.W. Wang, L.D. Zhang, G.Z. Wang, X.S. Peng, Z.Q. Chu, C.H. Liang, *J. Crystal growth* 234 (2002) 171.
- [16] Y. Wu, P. Yang, *Adv. Mater.* 13 (2001) 520.
- [17] C.C. Chen, C.C. Yeh, *Adv. Mater.* 12 (2000) 738.
- [18] R.A. Laudise, E.D. Kolb, A.J. Caporaso, *J. Am. Ceram. Soc.* 47 (1964) 9.
- [19] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.