Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Crystal Growth 274 (2005) 418–424
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Two-dimensional growth of ZnO epitaxial films on c-Al_2O_3 (0 0 0 1) substrates with optimized growth temperature and low-temperature buffer layer by plasma-assisted molecular beam epitaxy

Yeon-Sik Jung, Oleg Kononenko, Jin-Sang Kim, Won-Kook Choi*

Thin Film Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

Received 28 July 2004; accepted 7 October 2004
Communicated by D.P. Norton
Available online 21 November 2004

Abstract

High-quality ZnO thin films were deposited on *c*-plane sapphire substrates with the low-temperature (LT) ZnO homo-buffer layer by plasma-assisted molecular beam epitaxy. LT ZnO buffer layer with the thickness of 15 nm was grown at 500 °C. After high-temperature annealing at 800 °C for 30 min, the growth of ZnO with about 800 nm thickness was restarted at different temperatures from 680 to 800 °C. Although the surface of the LT-buffer layer was three-dimensional, appropriate subsequent growth temperature facilitated two-dimensional growth. The smallest full-width at half-maximum (FWHM) of X-ray ω-rocking for ZnO(0 0 0 2) diffraction was 85 arcsec and then slightly increased with the increament of the deposition temperature. The RHEED pattern over the surface of ZnO film grown at 720 °C showed very streaky lines, while streaky lines superimposed with spotty patterns were obtained at other temperatures. From the Hall measurement, the mobility values for the ZnO films deposited at 720 and 760 °C were 103 and 105 $cm^2/V\,s$, and the carrier concentration was 2.45×10^{17} and $2.21 \times 10^{17}/cm^3$, respectively. In low-temperature photoluminescence measurement at 10 K, most of the ZnO thin films showed neutral donor-bound exciton, $I_4(D^0, X)$ at 3.362 eV and acceptor-bound exciton, $I_{10}(A^0, X)$ at 3.3497 eV were clearly observed with the phonon replica at 3.308 eV, and the lowest FWFM of I_{10} peak was found to be 8.4 meV for the ZnO grown at 720 °C.

PACS: 61.10.Nz; 61.14.Hg; 68.55.Jk; 73.61.Ga; 78.66.Hf; 81.15.Hi

Keywords: A1. Crystal structure; A1. Photoluminescence; A1. Reflection high-energy electron diffraction; A1. X-ray diffraction; A3. Molecular beam epitaxy; B2. Semiconducting II–VI materials

*Corresponding author. Tel.: +82 2 958 5562; fax: +82 2 958 6681.
E-mail address: wkchoi@kist.re.kr (W.-K. Choi).

0022-0248/$ - see front matter
doi:10.1016/j.jcrysgro.2004.10.016

1. Introduction

ZnO has been noticed as a promising candidate for UV/Blue optical devices [1–3] since it was discovered that the luminescence mechanism of the near band-edge emission (NBE) and the green deep-defect level emission of ZnO are quite analogous to those of GaN [4]. Much interest, in particular, has been paid due to its large exciton-binding energy (59 meV) as compared to GaN (28 meV), and its higher optical gain ($300\,cm^{-1}$) than GaN ($100\,cm^{-1}$) at room temperature [5].

Low-temperature homo-buffer layers for epitaxial ZnO films deposited on sapphire substrates have been tried [4,6–8] to reduce the defects and dislocation density caused by the lattice misfit between ZnO *a*-axis and O sub-lattice of Al_2O_3, which is as large as 18.3%. Among them, the buffer layers grown with an appropriate thickness (15 nm) and a moderate deposition temperature (500 °C) showed better electrical, optical, and morphological properties in the previous work [8]. Meanwhile, some researchers have reported that depositing thin hetero-buffer layers such as MgO was an essential process for attaining the ZnO films of two-dimensional growth on *c*-sapphire substrates because MgO (1 1 1) has an intermediate in-plane lattice constant between ZnO (0 0 0 1) and Al_2O_3 (0 0 0 1), thus it effectively accommodated the abrupt lattice mismatch [9–13].

In this work, we report on two-dimensional growth of ZnO films without using hetero-buffer layer by controlling the growth temperature of high-temperature (HT-ZnO) films deposited on the low-temperature ZnO (LT-ZnO) buffer layer whose deposition and thermal treatment conditions were optimized. The morphological, electrical, and optical properties of the films were analyzed and compared with those of other reports about buffer layer deposition. Characterization tools such as reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), X-ray diffraction (XRD), photoluminescence (PL), and Hall measurement were used for the analysis.

2. Experimental procedure

The ZnO films were deposited on crystalline α-Al_2O_3(0 0 0 1) single crystal by plasma-assisted molecular beam epitaxy (PA-MBE). An elemental Knudsen cell was used to supply zinc atoms of 6 N purity and the temperature of the cell was maintained at 355 °C during deposition. Active oxygen species were generated and spread over the sapphire substrate through a radio-frequency (RF) plasma source activated at the power of 450 W. Before deposition, the *c*-plane sapphire substrates (MATEK) were cleaned with trichloroethylene, acetone, methanol, and ethanol, and then they were treated in the heated acid solution of H_2SO_4 and H_3PO_4 for 10 min [14]. After the substrate was transferred from the load-lock chamber to the main chamber (base pressure = $1–2 \times 10^{-9}$ Torr), the substrate was thermally cleaned at 800 °C for 30 min under an oxygen plasma atmosphere of 1×10^{-4} Torr. Low-temperature buffer layers with the thickness of 15 nm were grown at 500 °C, and were thermally treated at 800 °C for 30 min. Then, the growth was restarted at different temperatures from 680 to 720 °C and continued for 4 h. The total thickness of the films was about 800 nm. RHEED (Oxford Applied Research, LEG 110) patterns were observed to monitor the growth mode and surface status of the films during deposition. Photoluminescence and Hall measurements were performed to analyze optical and electrical properties, respectively. The surface morphology of the samples were characterized by an AFM (PSIA Co.). The crystalline quality of the deposited films was estimated by X-ray diffraction rocking curves (Bruker AXS, D8 Discover).

3. Results and discussion

Figs. 1a and b present the RHEED patterns from the surface of ZnO buffer layers with the thickness of 15 nm before and after the thermal treatment at 800 °C for 30 min, respectively. A 30° rotation in the basal plane of the ZnO buffer layer was observed by RHEED, and the $[1\bar{2}10]$ direction of ZnO was found to align with $[1\bar{1}00]$ direction of Al_2O_3 (1000). Both images show

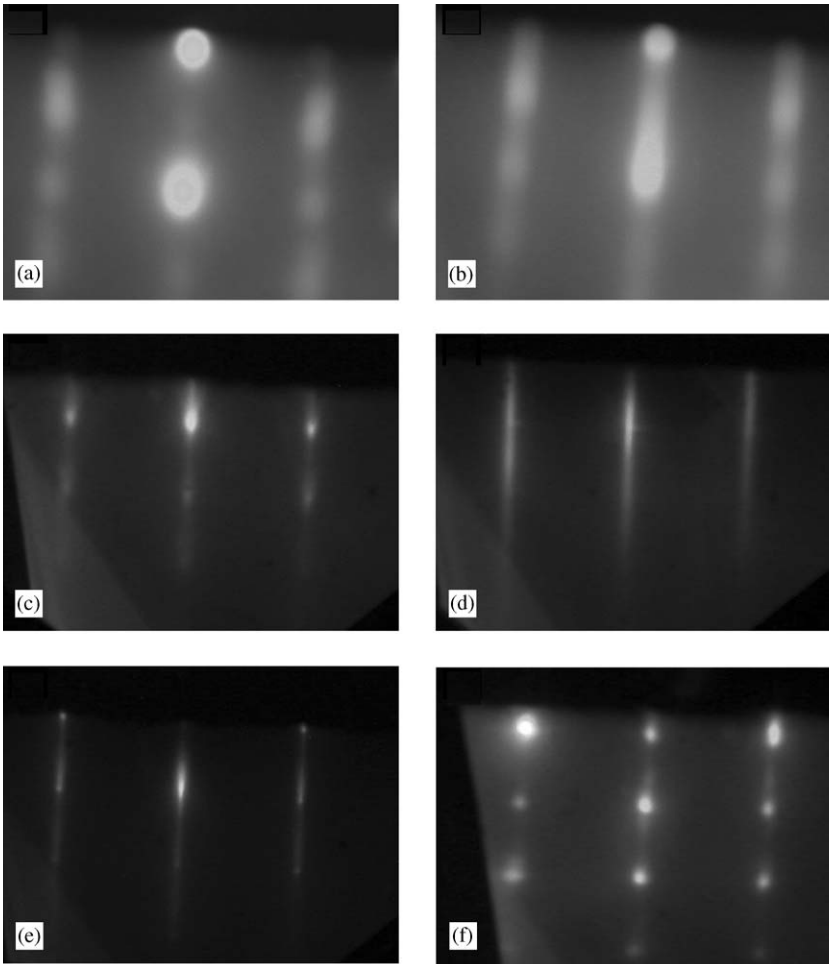

Fig. 1. $\langle 1\bar{2}10\rangle$ RHEED patterns of (a) LT-buffer layer 15 nm deposited at 500 °C and (b) after annealing the buffer layer for 30 min at 720 °C. Subsequent deposition of HT-ZnO at (c) 680, (d) 720, (e) 760, and (f) 800 °C.

mixed patterns composed of spots and streaks, however, the RHEED pattern of a thermally treated sample shows changing feature relatively closer to a streaky one, which means thermal treatment definitely contributes to the rearrangement of atoms into a smoother surface [8,12]. The optimized LT homo-buffer deposition and treatment conditions for subsequent deposition of HT-ZnO layer of high quality were reported in earlier work [8]. In previous work, where only the LT-ZnO buffer layer was used, the critical thickness and growth temperature of LT buffer layer and also thermal treatment conditions for obtaining a sharp and streaky RHEED pattern were not clearly revealed, and the RHEED pattern of the annealed buffer layer still included a diffused and spotty character. Moreover, the ZnO grown at 800 °C with 100 nm on the LT-buffer prepared at different growth temperature of 450–700 °C and thickness of 8–30 nm showed the high concentration of $6\times10^{18}/\mathrm{cm}^3$–$1.2\times10^{20}/\mathrm{cm}^3$ and the moderate mobility of $\mu = 40-57\,\mathrm{cm}^2/\mathrm{V\,s}$ because of the relatively small film thickness of 0.1 μm.

Figs. 1c–f show the RHEED patterns of the 800 nm-thick ZnO films with different growth temperatures from 680 to 800 °C. The ZnO films were deposited on the same ZnO buffer layers with the thickness of 15 nm, which was thermally treated at 800 °C for 30 min. The RHEED pattern of the ZnO film deposited at 680 °C showed a streaky pattern mixed with spots. At such a low temperature around 680 °C, the adatom mobility is thought to be still insufficient to achieve a two-dimensional growth mode. At a slight increased temperature of 720 °C, the RHEED pattern showed a very streaky pattern, which reveals atomically flat two-dimensional growth mode. These results indicate that ZnO films with two-dimensional growth mode can be attained with only LT homo-buffer layer and appropriate growth temperature without using hetero-buffer layers such as MgO or GaN, which were suggested to decrease unfavorable effects of the large lattice mismatch between *c*-sapphire substrates and ZnO films [9–13,15]. In other words, atomically flat buffer layer is not always a necessary condition for the two-dimensional growth of upper ZnO layer because a two-dimensional growth could be successfully achieved through the appropriate growth temperature of 720 °C on the annealed buffer layer not atomically flat. On the other hand, when the deposition temperature was further increased, the RHEED patterns turned into a more spotty shape again as shown in Figs. 1e and f. It can be merely surmised that the energy of adatom at 760–800 °C is so sufficient as to increase surface diffusion for the two-dimensional growth, but the comparatively high growth temperature might enhance the grain growth and in consequence the growth of ZnO thin film was changed into three-dimentional mode. At a high temperature, increase of surface roughness due to three-dimensional growth directly reflects on the formation of spotty feature in RHEED pattern.

The corresponding AFM images are shown in Figs. 2a–d. The calculated root-mean-square's (σ_{RMS}'s) of surface roughness values of the ZnO films with different deposition temperatures are shown in Fig. 2e. By increasing the deposition temperature, the AFM images show that the boundary lines seem to be more effectively filled up by atoms. As was mentioned already, the growth temperature of 720 °C provided the smoothest surface with $\sigma_{RMS} = 1.9$ nm over the scanned size of $2\mu m \times 2\mu m$ and $\sigma_{RMS} = 0.7$ nm within smaller scanned area, which is slightly larger than the reported one [11] of $\sigma_{RMS} = 0.3-0.4$ nm when annealed MgO buffer layers were employed. As can be seen, the surface roughness was increased after 720 °C and this can support the formation of spot pattern in RHEED.

Fig. 3 presents the XRD ω-rocking curve (XRC) of the ZnO (0 0 0 2) films deposited at 720 °C. The inset graph shows the calculated FWHM values of the ZnO films with different growth temperature. The full-width at half-maximum of XRC for the symmetric (0 0 0 2) diffraction implies the tilt component of the in-plane mosaic misorientation (tilt), which is well correlated with the density of screw dislocations. The film deposited at 720 °C showed the smallest FWHM of about 85 arcsec and it slightly increased to 90 arcsec for the film grown at 760 °C, which was much less than the ever reported value of 320 arcsec given by a pulsed laser deposition of ZnO films where the LT-ZnO buffer-layer was adopted [6]. This means that quite lower defects were incorporated in the film deposited at 720 °C due to a smooth and well-ordered surface structure of the two-dimensional growth mode. However, recent reports about the effect of double buffer, where an MgO and LT-ZnO buffer, were combined presents a much superior value as low as 18–41 arcsec [11,12].

Fig. 4 shows the electrical properties of ZnO films calculated by Hall measurement. As the temperature was increased from 680 to 720 °C, Hall mobility was enhanced from 54 to 103 $cm^2/V s$, and carrier concentration decreased from 6.83×10^{17} to $2.45 \times 10^{17}/cm^3$. Decreased defect concentration, which was identified by the FWHM of ω-rocking curves in Fig. 3, might result in a lower carrier density for the films grown at higher temperatures. The improved mobility of the film deposited at higher growth temperature can be attributed to the decreased concentration of scattering centers. These values are comparable to the high mobility and low carrier concentration values in the case of adopting MgO hetero-buffer layer [9]. Meanwhile, recently Miyamoto et al. reported improved mobility as a result of decreased deposition rate of LT-ZnO buffer on MgO

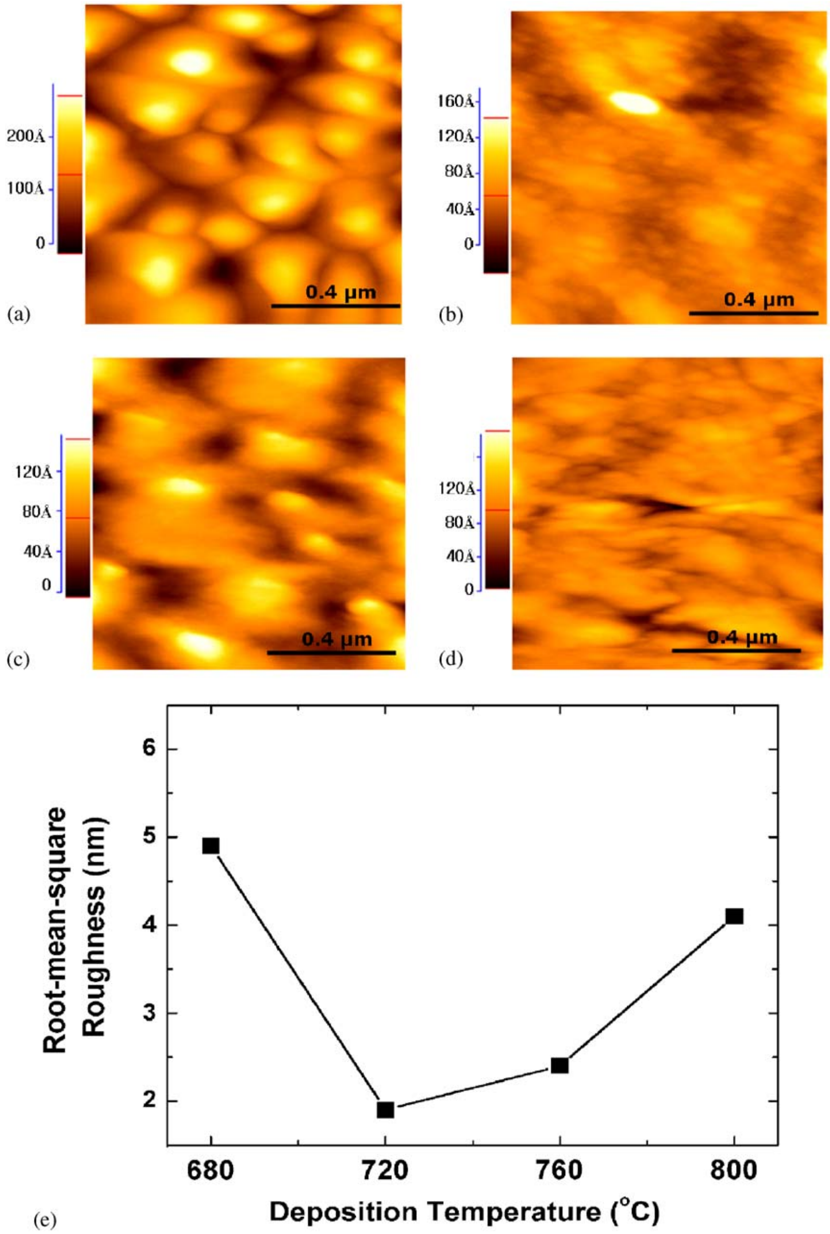

Fig. 2. AFM images of the ZnO films deposited at (a) 680 °C (b) 720 °C (c) 760 °C, and (d) 800 °C, respectively. (e) Calculated root-mean-square roughness of the ZnO films.

buffer by reducing the edge dislocations [11,13]. The Hall measurement of the ZnO film deposited at 800 °C could not be performed because of too high resistance of the sample. Two possibilities can be assumed, and they are of very low carrier concentration or very low mobility of the film. Considering the decrease of carrier concentration when increasing the deposition temperature from 680 to 760 °C, a further decrease of carrier concentration would be more closely related to

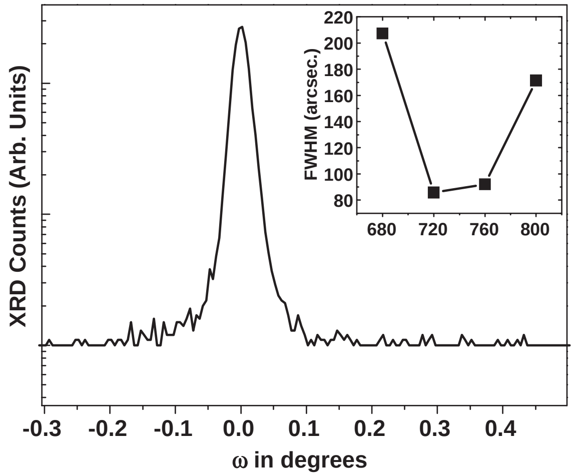

Fig. 3. XRD ω-rocking curves of the ZnO (0 0 0 2) films deposited with on Al_2O_3 (0 0 0 1) substrates with different growth temperatures.

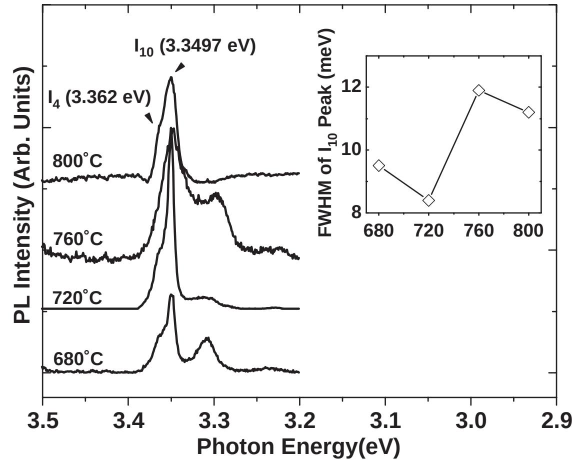

Fig. 5. Low-temperature (10 K) PL measurement results of the ZnO films on Al_2O_3 (0 0 0 1) substrates with different growth temperatures.

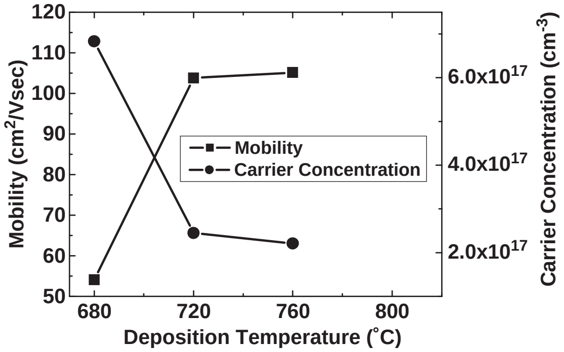

Fig. 4. Hall measurement results of the ZnO films deposited with on Al_2O_3 (0 0 0 1) substrates with different growth temperatures.

the increase of the resistance of the film deposited at high temperature rather than the contribution of relatively worse morphology and crystallinity of the film to poor mobility of the film.

Fig. 5 represents the low-temperature (10 K) PL spectra for the ZnO films deposited at 680–800 °C. The PL peaks from excitons bound to neutral donors I_4 (D^0,X), at 3.362 eV and bound to neutral acceptors I_{10}(A^0,X) at 3.497 eV were identified despite some obscurities still remaining in exact designation of bound exciton. Phonon replica of free exciton peak at 3.308 eV was also well observed except for the film grown at 800 °C. The peak intensity ratio I_4/I_{10}, which was obtained by decomposing the combined peaks, decreased from about 0.65 to 0.30 by the increment of deposition temperature from 680 to 720 °C. However, the decomposition of PL peaks from the samples deposited at 760 and 800 °C did not produce explicit peaks at 3.362 eV (I_4), which are related to donors. This might be correlated with the smaller n-type carrier concentration of the ZnO films deposited at higher temperatures. The film deposited at 720 °C showed the lowest FWHM of I_{10} peak of 8.4 meV and was believed optically to be of very high quality.

4. Conclusions

In this study, high-quality ZnO thin films were tried to be deposited using LT-ZnO homo-buffer layer through high-temperature vacuum annealing at 800 °C for 30 min, and the successive deposition at high temperature. ZnO thin films with a low concentration of $n = 2.2-2.45 \times 10^{17}/cm^3$ and high mobility 103–105 cm^2/V s could be obtained at deposition temperature of 720–760 °C. In particular the ZnO deposited at 720 °C showed the smallest FWHM of XRC for ZnO(0 0 0 2) of 85 arcsec. From the observation of $I_4(D^0,X)$ and $I_{10}(A^0,X)$ in PL at 10 K, the grown ZnO films at 720 °C were also believed to be of quite good quality for optical applications.

Acknowledgement

This work was financially supported by the KIST Future Resources Program Grant No. 2E18160.

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] X.L. Guo, J.H. Choi, H. Tabata, T. Kawai, Jpn. J. Appl. Phys. 40 (2001) L177.
[3] P. Yu, Z.K. Tang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Solid State Commun. 103 (1997) 459.
[4] K. Nakahara, H. Takasu, P. Fons, K. Iwata, A. Yamada, K. Matsubara, R. Hunger, S. Niki, J. Crystal Growth 227–228 (2001) 923.
[5] K. Hummer, Phys. Stat. Solidi. 56 (1973) 2.
[6] T. Nakamura, Y. Yamada, T. Kusumori, H. Minoura, H. Muto, Thin Solid Films 411 (2001) 60.
[7] K.H. Bang, D.K. Hwang, J.M. Myoung, Appl. Surf. Sci. 207 (2003) 359.
[8] Y.S. Jung, Y.S. No, J.S. Kim, W.K. Choi, J. Crystal Growth 267 (2004) 85.
[9] Y.F. Chen, H.J. Ko, S.K. Hong, T. Yao, Appl. Phys. Lett. 76 (2000) 559.
[10] Y.F. Chen, H.J. Ko, S.K. Hong, T. Yao, Y. Segawa, J. Crystal Growth 214–215 (2000) 87.
[11] K. Miyamoto, M. Sano, H. Kato, T. Yao, Jpn. J. Appl. Phys. 41 (2002) L1203.
[12] A. Setiawan, H.J. Ko, S.K. Hong, Y.F. Chen, T. Yao, Thin Solid Films 445 (2003) 213.
[13] K. Miyamoto, M. Sano, H. Kato, T. Yao, J. Crystal Growth 265 (2004) 34.
[14] Y. Chen, D.M. Bagnall, Z. Zhu, T. Sekiuchi, K.T. Park, K. Hiraga, T. Yao, S. Koyama, M.Y. Shen, T. Goto, J. Crystal Growth 181 (1997) 165.
[15] H.J. Ko, Y.F. Chen, S.K. Hong, T. Yao, J. Crystal Growth 209 (2000) 816.