Jpn. J. Appl. Phys. Vol. 41 (2002) pp. 28–31
Part 1, No. 1, January 2002
©2002 The Japan Society of Applied Physics

Effects of Thickness Variation on Properties of ZnO Thin Films Grown by Pulsed Laser Deposition

Jae-Min MYOUNG[1*], Wook-Hi YOON, Dong-Hi LEE[1], Ilgu YUN[2], Sang-Hyuck BAE[2] and Sang-Yeol LEE[2]

[1]*Information and Electronic Materials Research Laboratory, Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-Gu, Seoul 120-749, Korea*

[2]*Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-Gu, Seoul 120-749, Korea*

(Received July 9, 2001; accepted for publication October 22, 2001)

A series of ZnO films with various thicknesses were prepared on (0001) sapphire substrate by pulsed laser deposition (PLD). Scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis were utilized to investigate the effects of thickness variation on the surface morphology and the crystallinity. The electrical and optical properties of the films were also investigated as a function of the film thickness. It was found that the crystalline quality, electrical and optical properties of the films depended on the film thickness and were improved with increasing the film thickness. This is attributed to the fact that the films thinner than 4000 Å are under the severe misfit strain, which decreases with increasing the film thickness further. [DOI: 10.1143/JJAP.41.28]

KEYWORDS: ZnO, pulsed laser deposition (PLD), thickness variation, misfit strain, strain relaxation

1. Introduction

ZnO is a very attractive material for application to the optical devices such as blue-, violet-, and ultraviolet (UV)-light emitting diodes (LEDs) and laser diodes (LDs), since it has a direct and wide band gap of 3.3 eV at room temperature.[1,2] Moreover, owing to the large exciton binding energy (~60 meV), ZnO thin films exhibit very strong emissions by excitons even at room temperature.[3] Even though these advantages, the realization of optical devices based on ZnO is not reported yet since it is difficult to achieve *p*-type ZnO films.[4] Because of these difficulties, it has only been used for other applications such as transparent conducting electrodes in display devices, surface acoustic wave (SAW) devices, and solar cell windows.[5–7] However, recent progress in the crystal growth technique has led to the realization of high-quality epitaxial layers exhibiting room-temperature excitonic lasing, high-temperature excitonic stimulated emission, and homostructural *p–n* junctions.[8–10]

ZnO thin films have been deposited using a number of different techniques such as radio-frequency (RF) magnetron sputtering, metalorganic chemical vapor deposition (MOCVD), plasma-assisted molecular beam epitaxy (P-MBE), and PLD.[11–14] Among them, the PLD technique is very unique for the growth of oxide materials because the oxygen plasma created by the pulsed laser is very energetic and its density is easily controllable by changing the oxygen pressure. Up to date, there are several reports regarding the effect of oxygen pressure and growth temperature on the properties of ZnO films grown by PLD.[15,16] However, there has been no report on the effect of film thickness on properties of ZnO grown by PLD.

In this paper, we report on the effect of the thickness variation on the surface morphology and structural, electrical, and optical properties of ZnO thin films grown on *c*-plane sapphire by PLD. It is found that, as the film thickness increases, the crystallinity and optical and electrical properties of ZnO thin films are improved. Furthermore, ZnO films thicker than 4000 Å exhibit the near-bulk properties.

2. Experimental Procedure

ZnO films were deposited on (0001) sapphire substrates by PLD using a Nd:YAG pulsed laser with a wavelength of 355 nm. Sapphire substrates were degreased in successive rinses with acetone and methanol for 3 min. before being loaded into the chamber. The base pressure of the chamber was maintained at 1×10^{-6} Torr by turbomolecular pump. For the growth of ZnO thin films, the focused laser radiation illuminated a ZnO target rotated at 2 rpm to preclude pit formation in the target and ensure uniform ablation of the target.[17] The laser repetition rate and energy density were maintained at 5 Hz and 2.5 J/cm^2, respectively. The ceramic ZnO target with the purity of 99.999% and 1-in. diameter was used and, during deposition, the distance between the target and the substrate was fixed at 5 cm.

In order to investigate the effect of thickness variation on the properties of ZnO films, a series of films with various thicknesses were prepared at an oxygen (99.99%) pressure of 350 mTorr and at a substrate temperature of 400°C. After deposition, the film thicknesses measured by cross-sectional scanning tunneling microscopy (SEM) were 400, 1700, 4000, 9000 and 24000 Å, respectively. The surface morphology of the films was also monitored by SEM. The crystallinity of the films was investigated by the double-crystal x-ray diffractometry (DCXRD) using a Ni-filtered CuKα source. The x-ray diffraction scan in the $\theta/2\theta$ mode was performed to determine the film orientation along the film's surface normal, and the θ rocking curve measurements for (0002) diffraction were performed to determine the crystalline quality of the films. The electrical properties of the ZnO films were determined by van der Pauw Hall measurements at room temperature. Ohmic contacts were made by soldering indium on the film surface. A magnetic field of 5.53 kG was used in these measurements. To investigate the optical properties of ZnO films, photoluminescence (PL) measurements were performed using an Ar-ion laser which had an excitation wavelength of 351 nm and a power of 100 mW. All spectra were taken at room temperature by using a grating spectrometer and a photomultiplier tube (PMT) detector.

*E-mail address: jmmyoung@yonsei.ac.kr

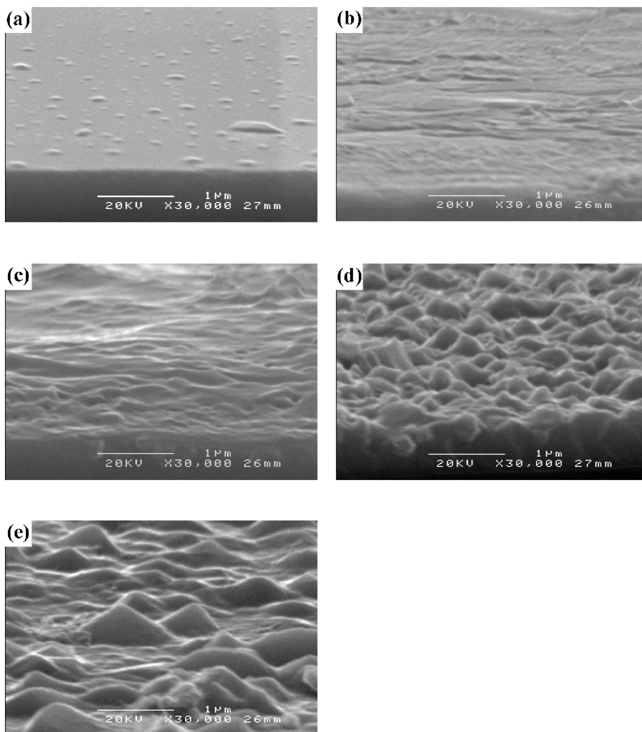

Fig. 1. SEM micrographs of the surfaces of ZnO films with different thickness of: (a) 400 Å, (b) 1700 Å, (c) 4000 Å, (d) 9000 Å, and (e) 24000 Å.

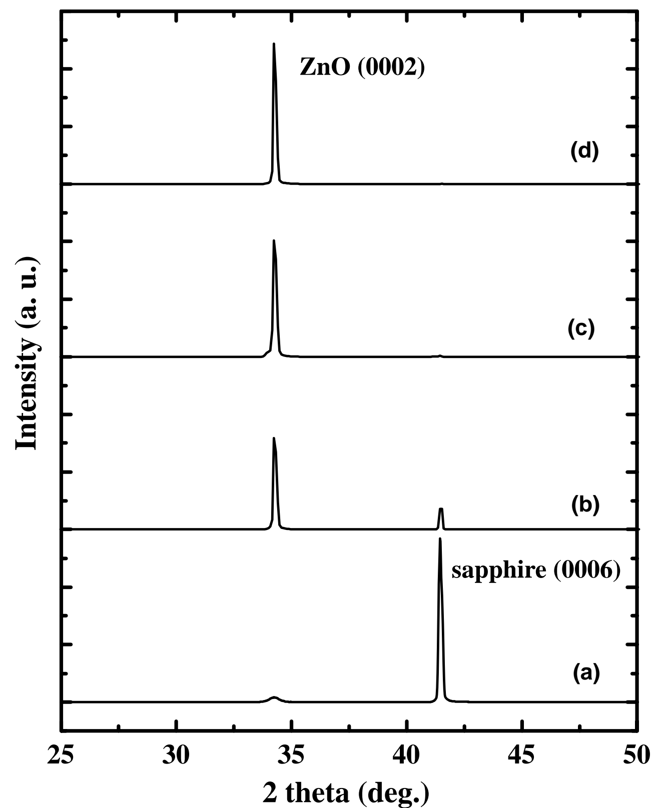

Fig. 2. XRD spectra of ZnO films with different thickness of: (a) 400 Å, (b) 4000 Å, (c) 9000 Å, and (d) 24000 Å.

3. Results and Discussion

Figure 1 shows SEM photographs of ZnO films with various thicknesses. It is observed that the surface morphology of the films varies with the film thickness. The samples with a thickness of 400 Å show a smooth surface with several islands [Fig. 1(a)] indicating the film growth in layer-plus-island mode. For the films with a thickness of 1700 and 4000 Å, a rough surface is observed as shown in Figs. 1(b) and 1(c), meaning the film growth in three-dimensional (3D) island mode. Further increase in the film thickness above 4000 Å leads very rough surface as shown in Figs. 1(d) and 1(e). Therefore, the samples with a thickness of 24000 Å exhibit several large grains. These facts are also confirmed by measurement of root-mean-square (rms) roughness determined by atomic force microscopy (AFM) (not shown). For the films with a thickness of 400 Å, the value of rms roughness is 3.2 nm indicating the film growth in layer-plus-island mode. However, as the film thickness increases from 1700 to 24000 Å, the value of rms roughness changes from 21 to 70 nm, indicative of a rough surface resulting from 3D island growth mode.

To investigate the crystalline quality of the films with various thicknesses, XRD analysis was made, and the results are shown in Fig. 2. All the films exhibit the ZnO (0002) diffraction since ZnO films grow with strong (0001) preferred orientation due to its lowest surface free energy.[11] The films with a thickness of 400 and 1700 Å exhibit the weak ZnO (0002) diffraction with a strong sapphire (0006) diffraction [Fig. 2(a)]. For both films, the position of the ZnO (0002) diffraction slightly shifts toward the higher-angle side than that of bulk ZnO, and it implies that both films are under tensile strain. As the film thickness increases to 4000 Å, the intensity of the ZnO (0002) diffraction increases and the shape of the diffraction peak sharpens as shown in Fig. 2(b). Finally, for the films with a thickness of 9000 and 24000 Å, strong (0002) diffraction peak is observed [Figs. 2(c) and 2(d)]. For both films, no shift in the ZnO (0002) diffraction angle is observed implying the tensile strain in the film is almost relaxed.

Figure 3 shows the full width at half maximum (FWHM) values of the double-crystal x-ray rocking curves (DCXRCs) for (0002) diffraction from ZnO films with various

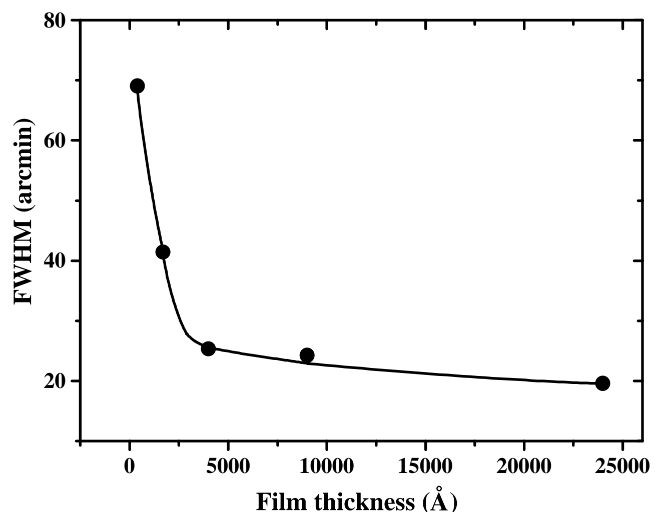

Fig. 3. FWHM values measured by DCXRC for (0002) diffraction from ZnO films with different thickness.

thicknesses. The films with a thickness of 400 Å show a large FWHM of 69 arcmin because of the large misfit strain between the film and the substrate. It is well known that, although ZnO and sapphire have the same crystal structure (wurtzite), there is a large lattice mismatch of 18% and it leads the large misfit strain in ZnO films. However, as the film thickness increases to 4000 Å, FWHM values exhibit sharp decrease, through 42 arcmin for a 1700-Å-thick film, to 25 arcmin for a 4000-Å-thick film. This result is attributed to the relaxation of the misfit strain with the formation of misfit dislocation in the films.[18] Therefore, as the film thickness increases, the misfit strain decreases resulting in better crystallinity. With increasing the film thickness further, FWHM values are saturated and the films having a thickness of 9000 and 24000 Å show FWHM values of 24 and 20 arcmin, respectively. This fact implies that, when the thickness of the films prepared by PLD is about 4000 Å, the misfit strain in the films is completely relaxed. Therefore, it is believed that the films thicker than 4000 Å exhibit the near-bulk material properties.

The electrical properties of the ZnO films were measured at room temperature and the results are shown in Fig. 4 as a function of the film thickness. All the films exhibit the *n*-type conductivity due to the *n*-type background carrier concentrations unintentionally introduced during the film deposition. The films with a thickness of 400 Å show the highest carrier concentration of $1.1 \times 10^{20}\,\mathrm{cm}^{-3}$, implying that the highest concentration of defects acting as donors is present in the films. However, as the film thickness increases to 4000 Å, auto-doped carrier concentration shows sharp decrease to $3 \times 10^{19}\,\mathrm{cm}^{-3}$ and, for the films thicker than 4000 Å, it is saturated at $\sim 8.6 \times 10^{18}\,\mathrm{cm}^{-3}$. This fact can be explained that, as the film thickness increases, better crystalline quality is achieved resulting in decrease of auto-doped defect concentration in the films. This result is in good agreement with DCXRC data in Fig. 3.

The room-temperature resistivities are also shown in Fig. 4. The films with a thickness of 400 Å exhibit the lowest resistivity of 0.002 Ω·cm, implying the most conductive films due to the highest carrier concentration. However, as the film thickness increases, the resistivity of the films increases since it is inversely proportional to the carrier concentration.

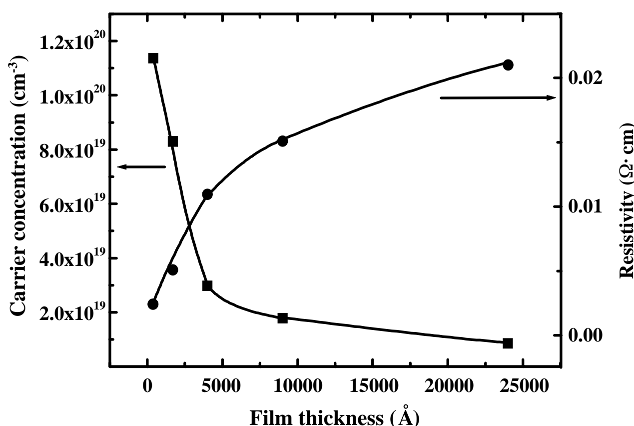

Fig. 4. Room-temperature electrical properties of ZnO films with different thickness determined by van der Pauw Hall measurements.

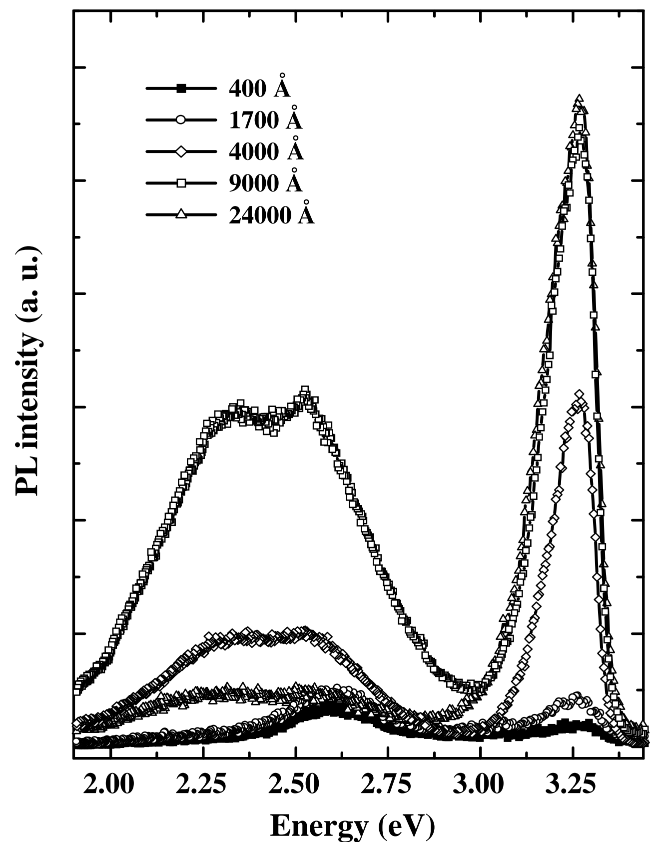

Fig. 5. PL spectra taken at room temperature for ZnO films with different thickness.

To investigate the optical properties of the films with various thicknesses, room-temperature PL measurements were performed, and the results are shown in Fig. 5. All the films exhibit both the near band-edge emission at ~3.27 eV and the deep-level emission around 2.5 eV. It is well known that the near band-edge emission corresponds to the recombination of excitons bound to donors.[19,20] However, the origin of the deep-level emission is not clearly understood yet. According to earlier studies, it might be attributed to both native defects like oxygen vacancies and impurities unintentionally introduced during the film deposition.[19–21] It is interesting to observe that, as the film is getting thicker, the intensity of the near band-edge emission increases. This result implies that the intensity of the near band-edge emission depends on the crystalline quality of the films shown in Fig. 3—better crystalline quality of the films leads to better optical properties. As was described already, the tensile strain in the films decreases with increasing film thickness resulting in better crystalline quality. On the other hand, as the film thickness increases to 9000 Å, the intensity of the deep-level emission increases, and the intensity ratio of the near band-edge emission to deep-level emission is less than 3. However, for the films with a thickness of 24000 Å, the intensity of the deep-level emission decreases, and the intensity ratio of the near band-edge emission to deep-level emission is about 12 indicating optically high-quality films.[20,21] Further study is required to fully understand the optical properties of ZnO films.

To investigate the effect of strain introduced in the film

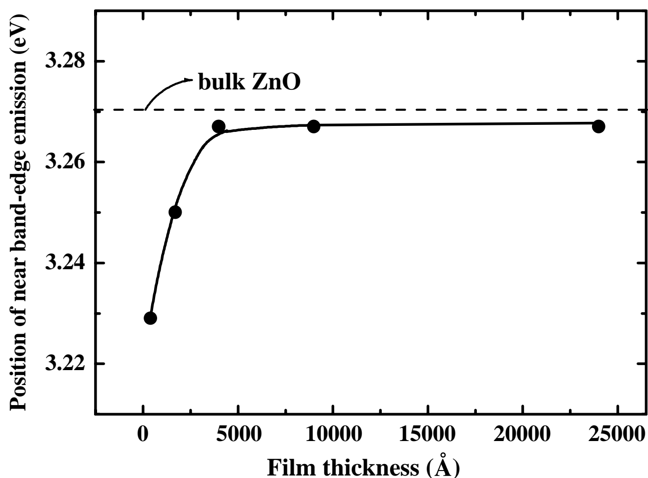

Fig. 6. Variation in the position of the near band-edge emission as a function of film thickness.

during the film deposition, the position of the near band-edge emission is plotted as a function of film thickness in Fig. 6. Earlier studies have reported that strain changes the interatomic spacing of semiconductors, then it affects the energy gap.[22] The near band-edge emission of bulk ZnO locates at 3.27 eV at room temperature. However, when the film is thin, the position of the near band-edge emission shifts toward the lower-energy side than that of bulk ZnO. The films with a thickness of 400 and 1700 Å exhibit the near band-edge emissions at 3.23 and 3.25 eV, respectively. It is attributed to the tensile strain in the film introduced during the film deposition. As the tensile strain in the film increases, the shift of the near band-edge emission increases indicating a 400-Å-thick film is under more severe strain than a 1700-Å-thick one. For the 4000-Å-thick film, the position of the near band-edge emission located at 3.267 eV indicating it is under slight tensile strain. With increasing the film thickness further, no change in the position of the near band-edge emission is observed implying the tensile strain in the film is almost relaxed. Furthermore, this fact is in good agreement with the results obtained by DCXRC and Hall measurements as shown in Figs. 3 and 4.

4. Conclusion

A series of ZnO films with various thicknesses were prepared on (0001) sapphire substrate by PLD. All the films show strong (0001) preferred orientation because of its lowest surface energy. It is found that the crystalline quality, electrical and optical properties of the films strongly depend on the film thickness and show large change around the film thickness of 4000 Å. Both FWHM values of DCXRC and carrier concentration determined by Hall measurements decrease with increasing the film thickness and, for the films thicker than 4000 Å, they are saturated. The RT-PL measurements show that, for the films thinner than 4000 Å, the position of the near band-edge emission exhibits large shift toward the lower-energy side while, for the films thicker than 4000 Å, it approaches to the value of bulk ZnO. These results are attributed to the fact that the films thinner than 4000 Å are under the severe tensile strain and it decreases with increasing the film thickness further. Therefore, it is believed that the films thicker than 4000 Å are almost strain-free and exhibit the near-bulk ZnO properties.

Acknowledgments

This work was supported in part by Yonsei University Research Board under Grant No. 2000-1-0161, and the Share-ISRC Program through Inter-University Semiconductor Research Center in the year of 2001.

1) V. Srikant and D. R. Clarke: J. Appl. Phys. **83** (1998) 5447.
2) D. C. Reynolds, D. C. Look, B. Jogai and H. Morkoc: Solid State Commun. **101** (1997) 643.
3) Hümmer: Phys. Status Solidi **56** (1973) 249.
4) Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong and H. W. White: J. Cryst. Growth **216** (2000) 330.
5) T. L. Yang, D. H. Zhang, J. Ma, H. L. Ma and Y. Chen: Thin Solid Films **326** (1998) 60.
6) M. H. Francombe and S. V. Krishnaswamy: J. Vac. Sci. Technol. A **8** (1990) 1382.
7) B. Sang, A. Yamada and M. Konagai: Jpn. J. Appl. Phys. **37** (1998) L206.
8) D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen and T. Goto: Appl. Phys. Lett. **70** (1997) 2230.
9) Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu and G. K. L. Wong: Phys. Status Solidi B **202** (1997) 669.
10) Y. R. Ryu, W. J. Kim and H. W. White: J. Cryst. Growth **219** (2000) 419.
11) N. Fujimura, T. Nishihara, S. Goto, J. Xua and T. Ito: J. Cryst. Growth **130** (1993) 269.
12) C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lu, M. Wraback and H. Shen: J. Appl. Phys. **85** (1999) 2595.
13) S. K. Hong, T. Hanada, H. J. Ko, Y. Chen, T. Yao, D. Imai, K. Araki and M. Shinohara: Appl. Phys. Lett. **77** (2000) 3571.
14) R. D. Vispute, V. Talyansky, R. P. Sharma, S. Choopun, M. Downes, T. Venkatesan, Y. X. Li, L. G. Salamanca-Riba, A. A. Iliadis, K. A. Jones and J. McGarrity: Appl. Surf. Sci. **127–129** (1998) 431.
15) B. J. Jin, S. Im and S. Y. Lee: Thin Solid Films **366** (2000) 107.
16) S. H. Bae, S. Y. Lee, B. J. Jin and S. Im: Surf. Sci. **154–155** (2000) 458.
17) Y. S. Jeong, S. Y. Lee, H. K. Jang, I. S. Yang, S. H. Moon and B. D. Oh: Appl. Surf. Sci. **109** (1997) 424.
18) K. N. Tu, J. W. Mayer and L. C. Feldman: *Electronic Thin Film Science For Electrical Engineers and Materials Scientists* (Macmillan, New York, 1992) Chap. 7, p. 161.
19) D. M. Bagnall, Y. F. Chen, M. Y. Shen, Z. Zhu, T. Goto and T. Yao: J. Cryst. Growth **184–185** (1998) 605.
20) S. Bethke, H. Pan and B. W. Wessels: Appl. Phys. Lett. **52** (1998) 138.
21) Y. R. Ryu, S. Zhu, J. D. Budai, H. R. Chandrasekhar, P. F. Miceli and H. W. White: J. Appl. Phys. **88** (2000) 201.
22) J. I. Pankove: *Optical Processes in Semiconductors* (Dover Publications, New York, 1971) Chap. 2, p. 22.