CUBIC GaN HETEROEPITAXY ON THIN-SiC-COVERED Si(001)

Yuichi Hiroyama , Masao Tamura

Joint Research Center for Atom Technology - Angstrom Technology Partnership,
1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan

Cite this article as: MRS Internet J. Nitride Semicond. Res. 4S1, G3.9(1999)

We have investigated the growth conditions of cubic GaN (-GaN) layers on very thin SiC-covered Si(001) by using gas-source molecular beam epitaxy as functions of SiC layer thickness, Ga-cell temperature and substrate temperature. Under the present SiC formation conditions on Si substrates by carbonization using C_2H_2 gas, the SiC layers with the thickness between 2.5 and 4 nm result in the epitaxial growth of -GaN on thus SiC-formed Si substrates. At the highest GaN growth rate of 110 nm/h (a Ga-cell temperature of 950 °C), -GaN layers grown at a substrate temperature of 700 °C show a nearly flat surface morphology and the fraction of included hexagonal GaN becomes negligible when compared to the results of -GaN layers grown under other conditions of Ga-cell and substrate temperatures. Thus obtained -GaN films have good performance in photoluminescence intensity although the FWHM of band-edge recombination peak is still wider (137 meV) than the reported values for the -GaN on 3C-SiC and GaAs.

INTRODUCTION

The combination of optoelectronic III-nitrides and highly advanced Si technology has the potential to be a key technology for fabricating optoelectronic integrated circuits. The luminescence in the blue and ultraviolet regions of GaN has attracted a lot of interest from many scientists and engineers. It has been reported that cubic GaN (-GaN) epitaxial films can be grown on GaAs(001) and 3C-SiC(001) substrates by chemical vapor deposition (CVD) [1] or gas-source molecular beam epitaxy (MBE) [2, 3]. The successful growth of -GaN on Si, however, has been reported only by a group from Boston University [4]. In a previous paper we reported that thin cubic SiC(-SiC) formation on Si(001) substrates is effective for the epitaxial growth of -GaN on Si(001) [5]. We confirmed that thin SiC layers not only play the role as a buffer layer to reduce the large lattice mismatch between Si and -GaN but also as a mask to protect the Si substrates against the irradiation of the active nitrogen, *e.g.*, the nitrogen radicals and atomic nitrogen those were supplied during GaN growth.

The SiC formation by using a carbonization technique on Si substrates has been studied as an initial process of heteroepitaxy of SiC on Si [6]. Carbonization using hydrocarbons is a very easy way to obtain SiC layers on Si substrates; in the conventional CVD the carbonization was performed by using C_3H_8 [7] as a source gas and at very high processing temperatures between 1000 and 1300 °C. On the other hand, it was reported that SiC was obtained at lower temperatures (750 - 1000 °C) using acetylene (C_2H_2) [8], although pit formation in Si substrates was also observed. However low temperature carbonization is desired not only for avoiding the high-density pit formation as much as possible but also for device fabrication. In this paper we report the optimum SiC formation and -GaN growth conditions, such as V/III ratios and substrate temperatures by RF-activated MBE. We also discuss the quality of -GaN layers.

EXPERIMENT

Hydrogen-terminated Si(001) substrates were placed into a preparation chamber (having a base pressure of about 5×10^{-8} Torr) which was connected to an MBE growth chamber (base pressure of about 5×10^{-11} Torr). The Si substrates were heated up to 850 to 950 °C for 1 to 10 min under a C_2H_2 pressure of 5×10^{-7} to 5×10^{-5} Torr in

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press

order to form SiC layers. The SiC-formed Si(001) substrates were then cooled down to room temperature and immediately transferred to the MBE growth chamber . They were then annealed at 1000 °C for 1 min and cooled down to a growth temperature of 600 to 900 °C. GaN films were grown using RF-MBE under the following growth conditions: the nitrogen gas flow rate was set at 2 sccm and the RF-power was set at 300 W. Gallium molecular beam was supplied to the substrate by using a Knudsen-cell operating at 850 to 1000 °C.

The surface morphology and the quality of GaN films were characterized by using in-situ reflection high energy electron diffraction (RHEED) and cross-sectional transmission electron microscopy (XTEM) as well as x-ray diffraction (XRD) measurements. Photoluminescence (PL) measurements were also carried out using a 325 nm beam from a He-Cd laser.

THIN SiC LAYER FORMATION

Figure 1 shows high-resolution XTEM (HRXTEM) micrographs of the substrates carbonized at 950 °C for 10 min under various C_2H_2 pressures. For a C_2H_2 pressure of 5×10^{-7} Torr small SiC islands were formed on the Si. A RHEED pattern of the as-grown SiC layer showed three-dimensional diffused spots, as seen in the inset of Fig. 1(a). For a C_2H_2 pressure of 5×10^{-6} Torr the surface morphology of the SiC became flat (Fig. 1(b)), and a streaky RHEED pattern was observed. The film thickness of the SiC was approximately 4 nm. With a higher C_2H_2 pressure of 5×10^{-5} Torr an approximately 5-nm-thick SiC layer was formed. The clear spotty pattern shown in the inset of the Fig. 1(c) indicates that the surface flatness of the SiC was more degraded than that of the SiC grown at a pressure of 5×10^{-6} Torr. As shown in Fig. 1(b), the spacing between two {111} planes of the SiC layer was approximately 0.25 nm by referring to the spacing of 0.31 nm between {111}Si and was almost the same as that of bulk -SiC. This indicates that the misfit between SiC and Si was almost completely relaxed by the generation of misfit dislocations in the SiC layer.

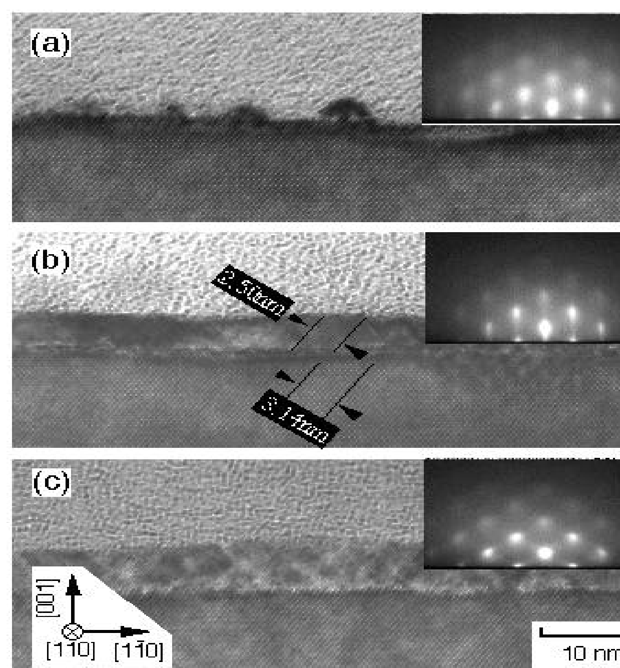


Figure 1. HRXTEM micrographs of the substrates carbonized at 950 °C for 10 min under various C_2H_2 pressures of (a) 5×10^{-7}, (b) 5×10^{-6} and (c) 5×10^{-5} Torr.

Figure 2 shows HRXTEM micrographs of Si substrates carbonized at 950 °C under a C_2H_2 pressure of 5×10^{-6} Torr for (a) 1 min and (b) 3 min. As seen in Fig. 2(a), a 1-nm-thick SiC layer was formed. The RHEED pattern of the SiC was more diffused than that of the thicker SiC layers. After carbonization for 3 min the thickness of the SiC layer was approximately 3 nm and the surface morphology was two-dimensional (Fig. 2(b)). Further growth of the SiC layer was saturated at 4 nm with the carbonization time up to 10 min as shown in Fig. 1(b). This thickness saturation of the SiC layer is known to be due to the suppression of the out-diffusion of Si atoms from the substrates during the SiC formation [9]. The GaN films grown on the substrates of Figs. 1(b), 1(c) and 2(b) became single-crystal cubic GaN films, while the films grown on the substrates shown in Figs. 1(a) and 2(a) became polycrystal structures having mixed phases of cubic and hexagonal GaN. Therefore, in order to avoid the degradation of the Si substrate as much as possible during the SiC formation, we employed the SiC formation conditions by short time heating for 3 min under a medium C_2H_2 pressure of 5×10^{-6} Torr.

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press

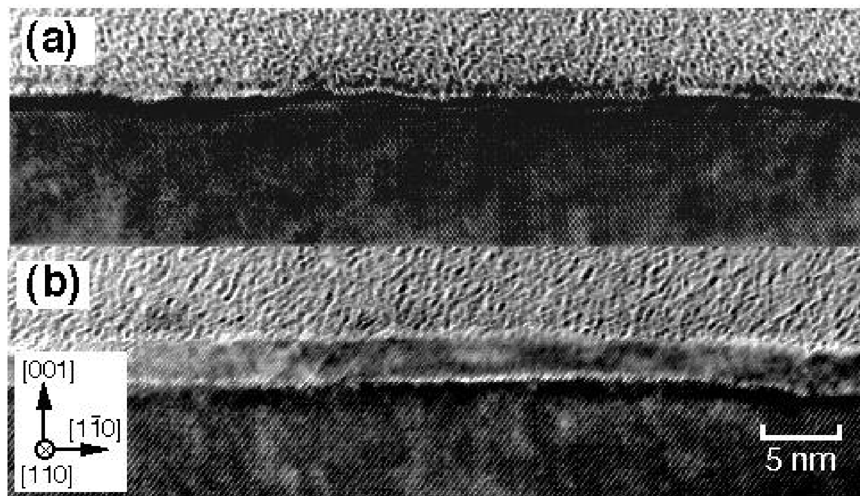


Figure 2. HRXTEM micrographs of Si substrates carbonized at 950 °C under a fixed C_2H_2 pressure of 5 × 10^{-6} Torr after annealing for (a) 1 and (b) 3 min.

GENERAL FEATURE OF GaN GROWTH

Figure 3 shows the GaN film growth rate as a function of Ga-cell temperatures (T_{Ga}) and substrate temperatures (T_{sub}). In the case of a constant T_{sub} the growth rate increased exponentially with the increase of T_{Ga} until it reached a saturation value of 110 nm/h at a T_{Ga} of 950 °C. This tendency was observed for all the T_{sub} cases from 600 to 800 °C. The growth rate at a T_{Ga} of 1000 °C was almost the same as that at 950 °C. This shows that the film growth at a T_{Ga} below 950 °C was dominated by the amount of Ga-flux (Ga-limited growth) and that the film growth at a T_{Ga} higher than 950 °C was dominated by the amount of N-flux (N-limited growth). Furthermore, in the case of a constant T_{Ga} below 930 °C the growth rate decreased with the increase of T_{sub}. This indicates that there was some loss of Ga by desorption during the growth with increased T_{sub}. With T_{Ga} of 950 °C and T_{sub} of 800 °C we concluded that the growth conditions of GaN were close to the stoichiometric conditions.

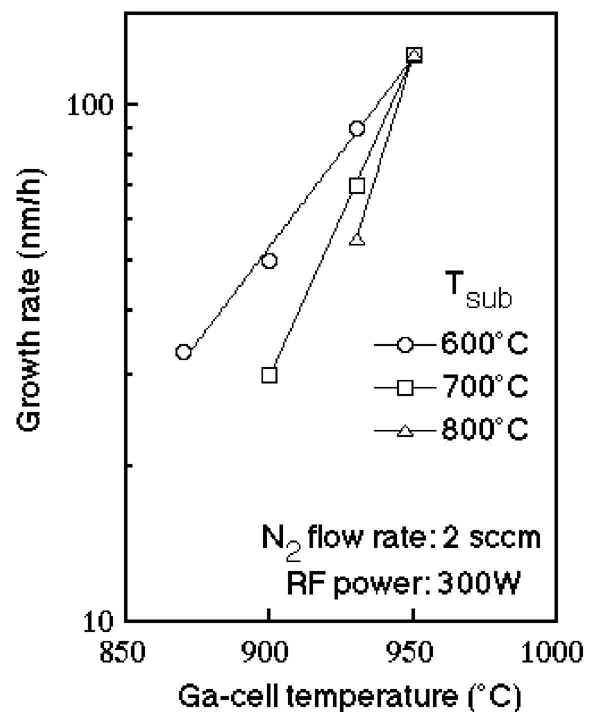


Figure 3. GaN film growth rate as a function of T_{Ga}.

Figure 4 shows RHEED patterns of GaN grown with different T_{sub} and T_{Ga} for [110] incidence of electron beams. All the patterns show that the GaN films basically have a -GaN structure, except for that grown at a T_{sub} of 900 °C. For a T_{Ga} of 870 °C the diffused ring-like pattern indicates that the grown layer consisted of grains that rotated on the (001) plane. For a T_{Ga} of 900 °C the ring-like pattern was obtained at a T_{sub} of 500 °C. With the increase of T_{sub} the pattern became sharper but showed extra weak spots due to the twin formation at a T_{sub} of 700 °C. For a higher T_{Ga} of 930 °C spotty patterns from -GaN were observed for all the T_{sub}. However, in the case of a T_{sub} of 600 and 800 °C, extra spots were included. At the highest T_{Ga} of 950 °C, spotty patterns were slightly elongated longitudinally for T_{sub} of 700 and 800 °C, which showed that the growing surface

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press

was rather flat. However, the spotty patterns at 900 °C mainly originated from a hexagonal structure together with clear rings due to the polycrystal formation.

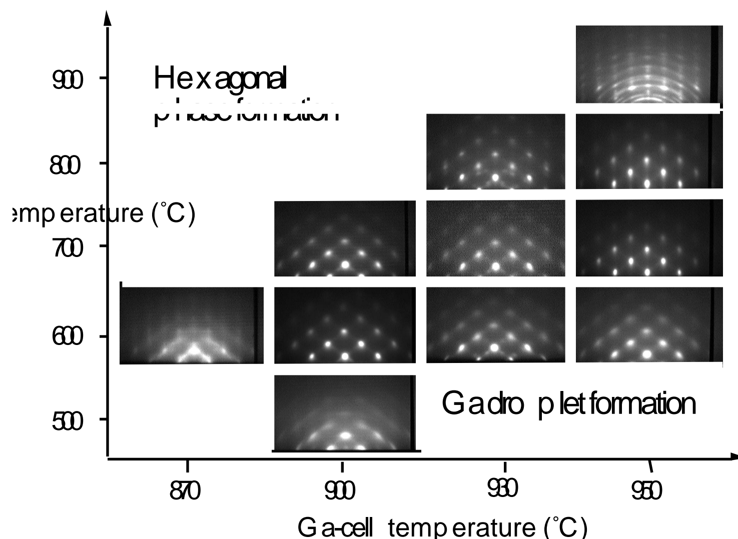
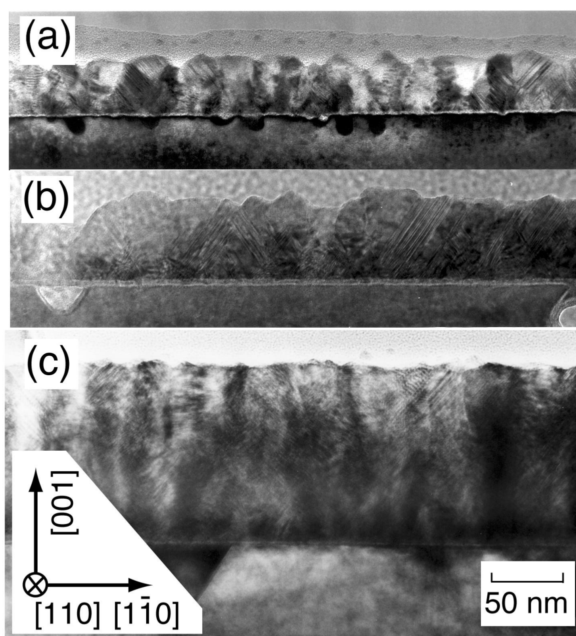


Figure 4. RHEED patterns of GaN grown at different T_{sub} and T_{Ga} for [110] incidence of electron beams.

CRYSTAL QUALITY

Figure 5 shows XTEM micrographs of the GaN grown at 600 °C for 1 hour with different T_{Ga}. At a T_{Ga} of 870 °C a columnar structure was clearly observed due to a large rotation angle of each column and the quality was much poorer than that of the higher T_{Ga} case. At a T_{Ga} of 900 °C the size of each column was larger than that at 870 °C and the boundary became unclear. At a T_{Ga} of 950 °C no columnar structure was observed and a nearly flat surface was obtained. With a higher T_{Ga}, for example, 1000 °C, the film growth rate did not increase as mentioned before and a Ga droplet formation on the surface became obvious due to the significant amount of excess Ga. These results suggest that the slightly Ga-rich conditions are favorable for the growth of -GaN on thin-SiC-covered Si(001).



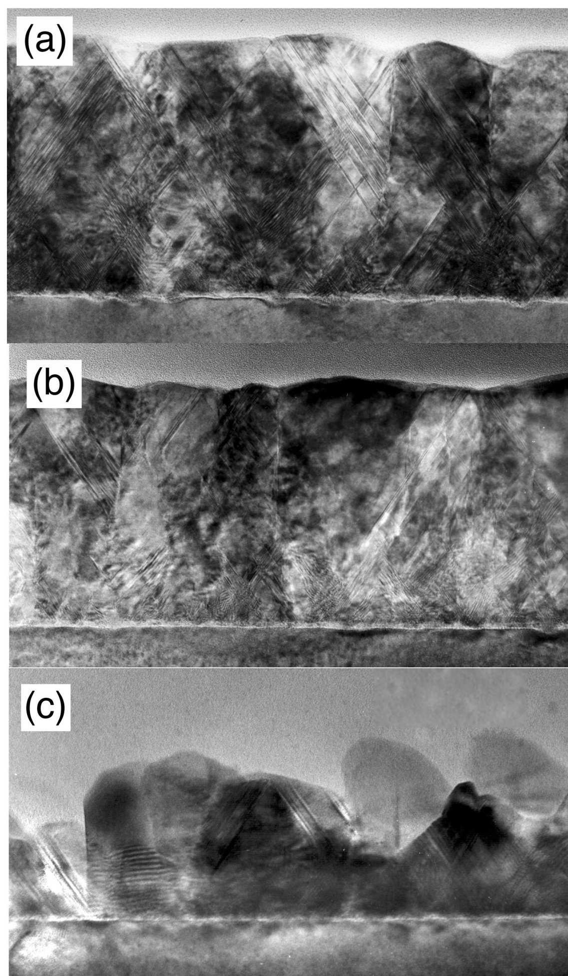


Figure 5. (upper) XTEM micrographs of the GaN grown at 600 °C for 1 hour with different T_{Ga}, (a) 870, (b) 900 and (c) 950 °C.

Figure 6. (right) XTEM micrographs of GaN films grown with T_{sub} of (a) 700, (b) 800 and (c) 900 °C. Ga-cell temperature was kept at 950 °C.

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press

Figure 6 shows XTEM micrographs of GaN films grown with various T_{sub}. The T_{Ga} was kept at 950 °C. In Fig. 6(a) and 6(b) no clear columnar structures were observed, although a number of stacking faults and twin boundaries were formed. At a T_{sub} of 900 °C, the quality of the GaN film became considerably worse, which coheres with the result of Fig. 4. This may be due to the enhancement of Ga desorption from the growing surface.

Long-time growth of GaN films was then carried out at T_{sub} of 700 and 800 °C. The T_{Ga} was fixed at 950 °C. The RHEED pattern of the 1.1-µm-thick film grown at 700 °C for 10 hours showed almost the same pattern as that after growth for 1 hour. On the other hand, the RHEED pattern of the sample grown at 800 °C for 10 hours showed the appearance of many extra spots, which indicated mixing of a hexagonal phase. From these results we concluded that the optimum T_{sub} and T_{Ga} are respectively 700 and 950 °C.

An XRD spectrum of the thick GaN had only one peak at 2 = 40.06° translating to the lattice spacing of (002)GaN as 2.25Å, which indicates that the grown GaN film was a single phase of -GaN. The full width at half maximum (FWHM) of the (002)GaN peak was 27 min. As listed in the ref. [10], the reported FWHMs of -GaN on GaAs and 3C-SiC was distributed in the range between 16 and 76 min.

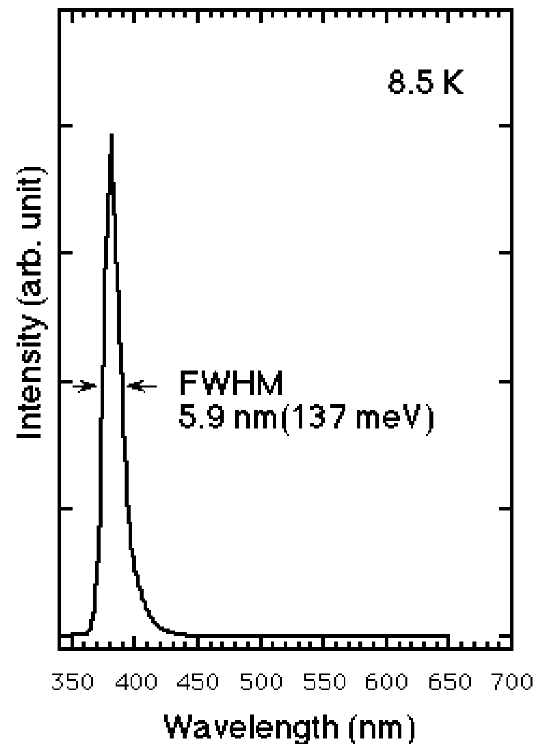


Figure 7. 8K PL spectrum of 1.1 µm-thick GaN.

Figure 7 shows an 8 K PL spectrum of a 1.1 µm-thick -GaN film grown under the optimum conditions; T_{Ga} and T_{sub} were at 950 and 700 °C, respectively. The PL spectrum was dominated by a near band-edge peak at 381 nm (3.25 eV). The FWHM of the 381 nm peak was approximately 5.9 nm (130 meV). The FWHM of our -GaN is wider than those obtained by Okumura et al. for -GaN on a 3C-SiC substrate using ECR-MBE (19 meV at 4.2 K) [10] and by As et al. for -GaN on a GaAs substrate using RF-MBE (24 meV at 2 K) [11]. The intensity of the yellow band between 500 and 700 nm, which is typically observed for hexagonal GaN, was 1000 times lower than that of the near band-edge peak at 381 nm. The donor-acceptor (D-A) recombination peak, reported to be around 400 nm for MOCVD [12] and gas-source MBE using hydrazine [10] and ammonia [13], was not observed in our -GaN.

CONCLUSIONS

We investigated the optimum growth conditions for obtaining cubic GaN on SiC-covered Si(001) by using RF-MBE. We found that SiC layers between 2.5 and 4 nm thick became flat and that single-crystal cubic GaN films could be grown on thus formed SiC layers. Under optimized growth conditions it was found, by XTEM observations and XRD measurements, that GaN has a flat surface and the amount of hexagonal GaN is negligibly small. The PL spectrum was dominated by a near band-edge peak at 381 nm whose FWHM was 5.9 nm.

ACKNOWLEDGEMENTS

The authors thank Dr. Tomoyoshi Mishima and Dr. Seiichi Isomae in Hitachi Central Research Laboratory for PL and XRD measurements. They also thank Dr. Masakazu Ichikawa and all members of the Ichikawa group of

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press

the JRCAT for fruitful discussions. This work, partly supported by NEDO, was performed in the JRCAT under the joint research agreement between ATP and NAIR.

REFERENCES

[1] M. Mizuta, S. Fujieda, Y. Matsumoto, T. Kawamura, Jpn. J. Appl. Phys. **25**, L945 (1986).
[2] M.J. Paisley, Z. Sitar, J.B. Posthill, RF. Davis, J. Vac. Sci. Technol. **A7**, 701 (1989).
[3] H. Okumura, S. Misawa, S. Yoshida, Appl. Phys. Lett. **59**, 1058 (1991).
[4] For example, T.D. Moustakas, T. Lei, R.J. Molnar, Physica **B185**, 36 (1993).
[5] Y. Hiroyama and M. Tamura, Jpn. J. Appl. Phys. **37**, L630 (1998).
[6] P. Pirouz, F. Ernst, T.T. Cheng, Mater. Res. Soc. Proc. **116**, 57 (1988).
[7] S. Nishino, J.A. Powell, H.A. Will, Appl. Phys. Lett. **42**, 460 (1983).
[8] H. Nagasawa and Y. Yamaguchi, J. Cryst. Growth **115**, 612 (1991).
[9] A.J. Steckl and J.P. Li, Thin Solid Films **216**, 149 (1992).
[10] H. Okumura, K. Ohta, G. Feuillet, K. Balakurishnan, S. Chichibu, H. Hamaguchi, P. Hacke, S. Yoshida, J. Cryst. Growth **178**, 113 (1997).
[11] D.J. As, F. Schmilgus, C. Wang, B. Schöttker, D. Schikora, K. Lischka, Appl. Phys. Lett. **70**, 1311 (1997).
[12] J.N. Kuzunia, J.W. Yang, Q.C. Chen, S. Krishnankutty , M. Ashif Khan, Appl. Phys. Lett. **65**, 2407 (1994).
[13] H. Okumura, S. Yoshida, T. Okahisa, Appl. Phys. Lett. **64**, 997 (1994).

https://doi.org/10.1557/S1092578300002386 Published online by Cambridge University Press