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GaN nanowires sputtered with Ag shell layers

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ABSTRACT

We have demonstrated the fabrication of GaN-core/Ag shell nanowires and investigated their annealing effects. Scanning electron microscopy has revealed that the thermal annealing facilitated the surface-roughening of the heteronanowires. TEM investigations indicated that the thermal annealing has changed the shell morphology from continuous Ag layer to the discrete Au nanoparticles or islands. X-ray diffraction suggested that the thermal annealing has enhanced the crystallinity of Ag shell. Photoluminescence measurements revealed that the Ag-sputtering has induced an UV peak, in addition to the GaN-associated emission peaks. Thermal annealing has further changing the overall shape of the PL spectrum and we have discussed the possible emission mechanisms.

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1. Introduction

Nanowires have attracted an extensive attention due to their specific physical and chemical properties and their potential applications as building blocks for nanoscale devices [1]. In order to enhance their functionalities as well as to protect them from contamination or oxidation, radial heterostructured nanowires have been created [2].

Hexagonal gallium nitride (GaN) has potential application in blue and ultraviolet light-emitting diodes and laser diodes, high temperature and high power optoelectronic devices [3,4] and thus the synthesis of GaN nanowires is a promising approach for future nanodevices [5,6]. Silver (Ag), with its highest electrical and thermal conductivities [7], has been used in a variety of applications, including catalysis [8], gas sensing [9], and optoelectronics [10]. Furthermore, Ag has been a favored coating material because it reveals optical response (plasmons) in the visible region [11].

GaN-based light-emitting diodes (LEDs) are crucial for the realization of solid-state lighting [12]. In the flip-chip LED geometry which can enhance the light extraction efficiency [13,14], p-type electrodes having good reflectance as well as low contact resistivity are required. Ag is known to be the most promising reflector, owing to its high reflectivity and relatively good ohmic behavior [15]. Also, Ag interlayer was brought in the metal contacts/p-GaN interface, in order to improve the ohmic characteristics [16]. In addition, it is known that Ag-coating increases the intensity of some modes in the Raman spectrum of GaN nanocrystals [17]. In recent years, GaN-based nanowires have been developed for high-efficiency LEDs [18,19] and

thus the characteristics of Ag coating on GaN nanowires need to be intensively studied.

In this study, we have coated the core GaN nanowires with Ag shell layers by using the plasma sputtering technique. The protective sheath made of Ag will not only prevent the degradation but also enhance the performance of core GaN nanowires. With the intrinsic properties of the Ag nanostructures being tailored by controlling its size, shape, and crystallinity [20], we have generated Ag nanoparticles by the subsequent thermal annealing of the heteronanowires.

2. Experimental

Core GaN nanowires were fabricated on silver (Ag: about 10 nm)-coated Si substrates by heating pure GaN powders in a tube furnace. During the experiment at the preset reaction temperature of 1000 °C, a mixture of Ar (flow rate: 100 sccm) and NH₃ (flow rate: 20 sccm) gases was flowed. The growth time was 60 min. Following this, the substrates were transferred to a turbo sputter coater with circular Ag target installed (Emitech K575X, Emitech Ltd., Ashford, Kent, UK) [21]. At room temperature, the sputter time was set to 1 min in high-purity argon (Ar) gas (99.999%). The DC sputtering current was set to 65 mA. Subsequently, as-fabricated samples were annealed for 30 min at 400–800 °C in N₂ ambient.

The size, structure, and composition of the products were investigated by powder X-ray diffraction (XRD, Philips X'pert MRD diffractometer), scanning electron microscopy (SEM, Hitachi, S-4200), transmission electron microscopy (TEM, Philips CM-200), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDS). The photoluminescence (PL) measurements were conducted by using the 325-nm line of a He–Cd laser as an excitation wavelength. The output laser power was 55 mW.

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3. Results and discussion

Fig. 1a and b shows SEM images of the as-synthesized and annealed core/shell nanowires. Although both products consist of one-dimensional (1D) structures, it is noteworthy that the surface of the nanowires became rough after thermal annealing at 600 °C. Fig. 2a and b shows a TEM image and a corresponding SAED pattern of an as-fabricated GaN-core/Ag-shell nanowire, respectively. The pattern showed diffraction rings of cubic Ag. In a lattice-resolved TEM image (Fig. 2c), the interplanar spacings of 0.235 nm correspond to the (111) plane of cubic Ag, indicating that the nanowire is poly-crystalline. The inset of Fig. 2c shows a typical EDX spectrum, revealing that the nanowires comprise Ag elements.

Fig. 3a shows a TEM image of a GaN-core/Ag-shell nanowire annealed at 600 °C. By comparing Fig. 3a with Fig. 2a, the Ag films have been transformed into particle-like structures as a result of the thermal annealing. Fig. 3b and c is EDX spectra from the region indicated by arrow 1 and arrow 2, respectively, in Fig. 3a, suggesting that the blacked regions in Fig. 3a correspond to the Ag-related particles. Fig. 3d is a lattice-resolved TEM image enlarging the area enclosed by the dotted box in Fig. 3a. In the blackened region, the marked parallel fringes with spacing of 0.235 nm correspond to the (111) plane of cubic Ag. On the other hand, in the outer region of the black particle-like region, two perpendicular interplanar distances with 0.26 nm match well with the d_{002} of the hexagonal GaN phase. The upper left inset shows the associated SAED pattern, confirming the existence of hexagonal GaN phase as well as the polycrystallites of the cubic Ag.

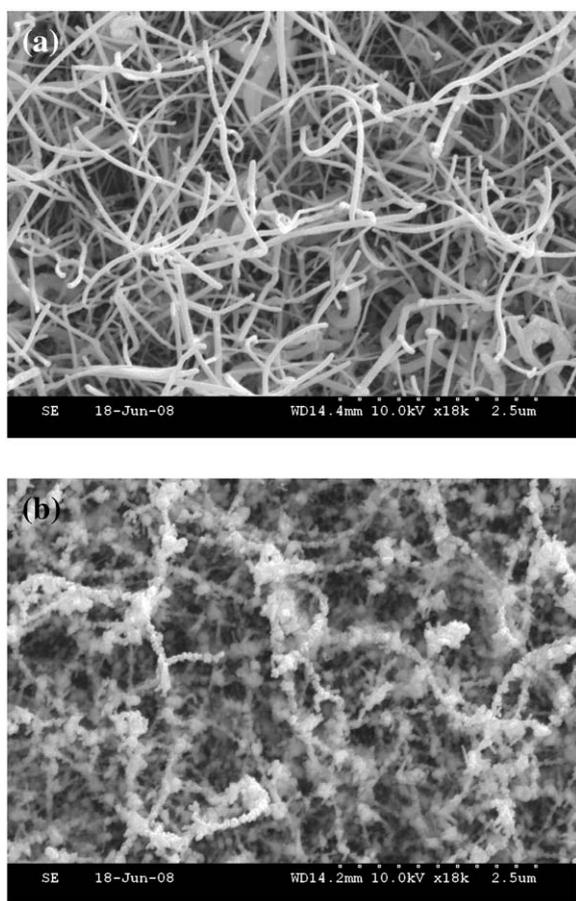


Fig. 1. SEM images of the core/shell nanowires (a) before and (b) after the thermal annealing at 600 °C.

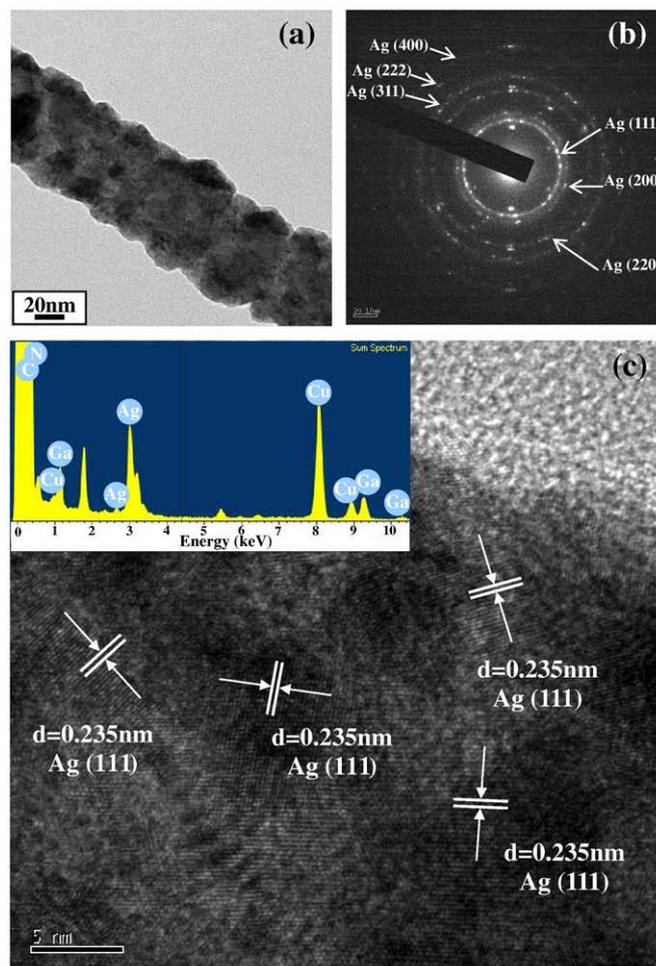


Fig. 2. (a) TEM image of an as-synthesized GaN-core/Ag-shell nanowire. (b) Corresponding SAED pattern image. (c) Lattice-resolved TEM image enlarging an area near the surface of the nanowires in (a). The inset exhibits an EDX spectrum which reveals the existence of Ag elements.

Fig. 4a shows an XRD pattern of core GaN nanowires, indicating that the whole spectrum can be indexed in peak position to a crystalline hexagonal wurtzite GaN phase (JCPDS card: No. 02-1078). Fig. 4b shows an XRD pattern of as-fabricated GaN-core/Ag-shell nanowires. It can be observed that there exists a cubic Ag phase (JCPDS card: No. 04-0783), as well as the GaN phase. On the other hand, Fig. 4c shows an XRD spectrum of GaN-core/Ag-shell nanowires which have been annealed at 600 °C. By comparing Fig. 4c with b, we reveal that the relative intensity of Ag-associated peak to GaN-related peaks is increased by thermal annealing at 600 °C.

Fig. 5a shows the normalized PL spectrum of core GaN nanowires prior to Ag coating, measured at room temperature. This emission can be deconvoluted into three peaks, centered at 2.9 eV in the blue region, 2.4 eV in the green region, and 1.9 eV in the red region, respectively. Green and blue emissions are attributed to vacancy-related structural defects, including V_{Ga} , $V_{Ga}-O_N$ complexes [22–25]. On the other hand, red emission band in GaN is generally attributed to the native defects such as vacancies or native interstitial atoms, possibly paired with the impurities [26–28]. In particular, C and O in GaN played a role in the red band [28,29], in which a donor–acceptor pair (DAP) transition process involving a deep donor $V_N C_N$ and a deep acceptor $V_{Ga} O_N$ has been suggested [29,30]. Although further study is in progress, dopant has not been intentionally introduced in our

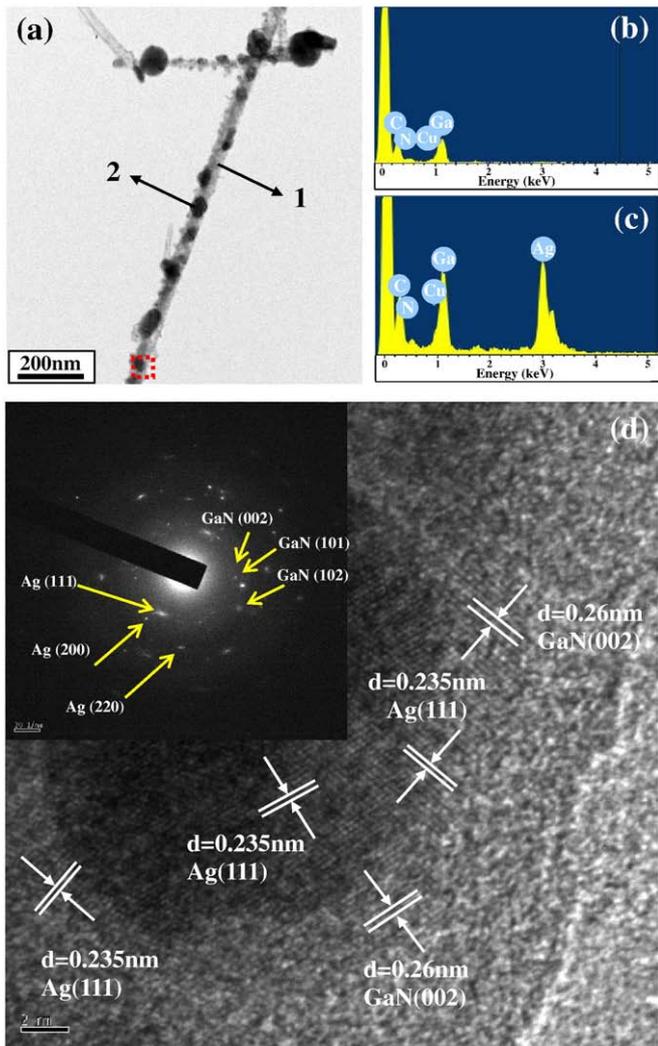


Fig. 3. TEM image of a GaN-core/Ag-shell nanowire annealed at 600 °C. (b,c) EDX spectra from the region indicated by (b) arrow 1 and (c) arrow 2, respectively, in (a). (d) Lattice-resolved TEM image enlarging an area enclosed by the dotted box in (a). The corresponding SAED pattern image is shown in the inset.

synthesis environment and thus the origin of red emission can be related to the impurities such as C and O, which might originate from inside the chamber during the synthetic process.

Fig. 5b shows the normalized PL spectrum of GaN-core/Ag-shell nanowire prior to thermal annealing. Apart from 2.9 eV-centered, 2.4 eV-centered, and 1.9 eV-centered peaks from GaN core, there exists an ultraviolet (UV) peak at around 3.3 eV. The UV peak was previously observed from Ag nanocrystals [31] and Ag nanoparticles [32], being attributed to the radiative decay of surface plasmon [31]. On the other hand, an UV emission was observed from the Ag-capped Si nanowires, which is attributed to Ag vacancy defects [33].

Fig. 5c shows the normalized PL spectrum of Ag-coated GaN nanowires after the thermal annealing at 800 °C. Being similar to unannealed sample (Fig. 5b), the emission spectrum exhibited four peaks, which are centered at 1.9 eV, 2.4 eV, 2.9 eV, and 3.3 eV. By the way, by comparing Fig. 5c with b, we note that the relative intensity of UV emission (3.3 eV) to visible emissions (1.9 eV, 2.4 eV, and 2.9 eV) was decreased by the thermal annealing at 800 °C. In order to investigate further, we have compared the PL intensity of unannealed and 800 °C-annealed samples in Fig. 5d. It can be observed that the

intensity of visible emissions is overall increased, whereas that of UV emission remains unchanged by the thermal annealing at 800 °C. If the UV emission is related to the Ag defects, the intensity should have been increased by the thermal annealing at a sufficiently high temperature. Accordingly, we surmise that the UV emission is mainly dominated by surface plasmon mechanism, in which the emission arises from the radiative recombination of *sp*-band electrons with *d*-band holes in Ag shell layers of clusters [31]. On the other hand, in the present study, high-temperature annealing process can generate various vacancy or vacancy-related complexes, contributing to the enhancement of both green and blue emissions. Furthermore, high temperature annealing may facilitate not only the generation of vacancy but also the introduction of C and O to the product, ultimately enhancing the red emission.

4. Conclusions

In summary, we have fabricated GaN-core/Ag-shell nanowires, for investigating the effects of thermal annealing on the structural and optical properties. Thermal annealing facilitates the generation of crystalline Ag nanoparticles. Gaussian deconvolution study reveals that the coating of Ag added a UV emission band to the PL spectrum of core GaN nanowires, which comprises 1.9 eV, 2.4 eV, and 2.9 eV-bands. The relative intensity of the visible bands to the UV band in the PL spectra is increased by the thermal annealing at 800 °C. We suggest

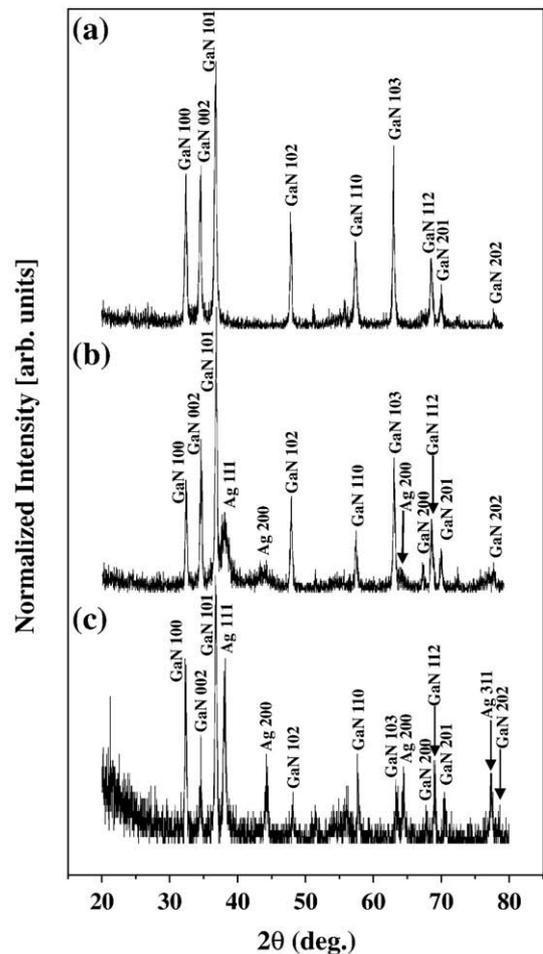


Fig. 4. XRD patterns of (a) core GaN nanowires, (b) as-synthesized GaN-core/Ag-shell nanowires, and (c) 600 °C-annealed GaN-core/Ag-shell nanowires.

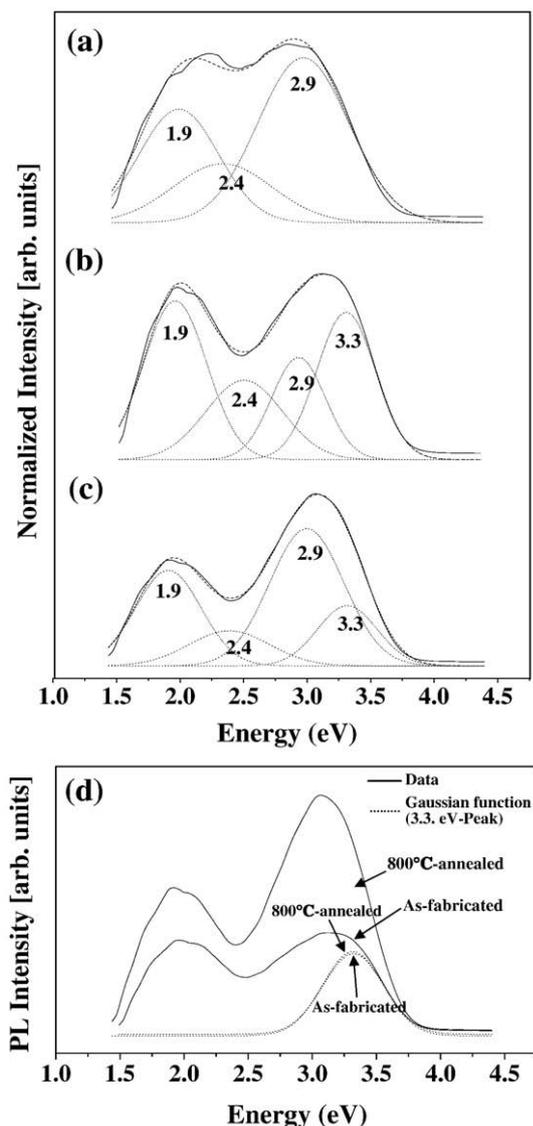


Fig. 5. Normalized PL spectra of (a) core GaN nanowires prior to Ag coating, (b) Ag-coated GaN nanowires prior to thermal annealing, and (c) Ag-coated GaN nanowires after thermal annealing at 800 °C. (d) Comparison of PL intensity between as-fabricated and 800 °C-annealed GaN-core/Ag-shell nanowires.

that the annealing-induced change in PL spectrum is associated with structural change in the GaN core nanowires.

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References

- [1] Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim, Y.Q. Yan, *Adv. Mater.* 15 (2003) 353.
- [2] L.J. Lauhon, M.S. Gudiksen, C.L. Wang, C.M. Lieber, *Nature* 420 (2002) 57.
- [3] J. Zolper, R. Shul, A. Baca, R. Wilson, S. Pearton, R. Stall, *Appl. Phys. Lett.* 68 (1996) 2273.
- [4] B. Liu, Y. Bando, C. Tang, F. Xu, J. Hu, D. Golberg, *J. Phys. Chem. B* 109 (2005) 17082.
- [5] H.M. Kim, Y.H. Choo, H. Lee, S.I. Kim, S.R. Ryu, D.Y. Kim, T.W. Kang, K.S. Chung, *Nano Lett.* 4 (2004) 1059.
- [6] Y. Huang, X. Duan, Y. Cui, C.M. Lieber, *Nano Lett.* 2 (2002) 101.
- [7] J.-Q. Hu, Q. Chen, Z.-X. Xie, G.B. Han, R.-H. Wang, B. Ren, Y. Zhang, Z.-L. Yang, Z.-Q. Tian, *Adv. Funct. Mater.* 14 (2004) 183.
- [8] A.N. Pstryakov, N.E. Bogdanchikova, A. Knop-Gericke, *Catal. Today* 91–92 (2004) 49.
- [9] H. Matsuura, Y. Sato, T. Sawaguchi, F. Mizutani, *Sens. Actuators, B* 91 (2003) 148.
- [10] B. Jin, Y. Cao, C.A. Lirkin, K.L. Kelly, G.C. Schatz, J.G. Zheng, *Science* 294 (2001) 1901.
- [11] T. Tuval, A. Gedanken, *Nanotechnology* 18 (2007) 255601.
- [12] S. Nakamura, T. Mukai, M. Senoh, *Appl. Phys. Lett.* 64 (1994) 1687.
- [13] Y.T. Hwang, H.-G. Hong, T.-Y. Seong, D.-S. Leem, T. Lee, K.-K. Kim, J.-O. Song, *Mater. Sci. Semicond. Process.* 10 (2007) 14.
- [14] H.-G. Hong, J.-O. Song, T. Lee, I.T. Ferguson, J.S. Kwak, T.-Y. Seong, *Mater. Sci. Eng. B* 129 (2006) 176.
- [15] D.L. Hibbard, S.P. Jung, C. Wang, D. Ullery, Y.S. Zhao, H.P. Lee, W. So, H. Liu, *Appl. Phys. Lett.* 83 (2003) 311.
- [16] J.-O. Song, J.S. Kwak, T.-Y. Seong, *Semicond. Sci. Technol.* 21 (2006) L7.
- [17] V.N. Bessolov, E.V. Kononkova, Y.u.V. Zhilyaev, B.A. Paez Sierra, D.R.T. Zahn, *Appl. Surf. Sci.* 235 (2004) 274.
- [18] F. Qian, S. Gradecak, Y. Li, C.-Y. Wen, C.M. Lieber, *Nano Lett.* 5 (2005) 2287.
- [19] Y. Huang, X. Duan, C.M. Lieber, *Small* 1 (2005) 142.
- [20] Y. Sun, B. Mayers, Y. Xia, *Nano Lett.* 3 (2003) 675.
- [21] H.W. Kim, S.H. Shim, J.W. Lee, *Carbon* 45 (2007) 2695.
- [22] M.A. Reshchikov, H. Morkoc, S.S. Park, K.Y. Lee, *Appl. Phys. Lett.* 78 (2001) 3041.
- [23] M.A. Reshchikov, H. Morkoc, *J. Appl. Phys.* 97 (2005) 061301.
- [24] M.A. Reshchikov, R.Y. Korotkov, *Phys. Rev. B* 64 (2001) 115205.
- [25] H.C. Yang, T.Y. Lin, Y.F. Chen, *Phys. Rev. B* 62 (2000) 12593.
- [26] S. Nakamura, N. Iwasa, M. Senoh, T. Mukai, *Jpn. J. Appl. Phys.* 31 (1992) 1258.
- [27] U. Kaufmann, M. Kunzer, H. Obloh, M. Maier, C.h. Manz, A. Ramakrishnan, B. Santic, *Phys. Rev. B* 59 (1999) 5561.
- [28] D.M. Hofmann, B.K. Meyer, H. Alves, F. Leiter, W. Burkhard, N. Romanov, Y. Kim, J. Krüger, E.R. Weber, *Phys. Status Solidi (a)* 180 (2000) 261.
- [29] L. Wang, E. Richter, M. Weyers, *Phys. Status Solidi (a)* 204 (2007) 846.
- [30] S. Zeng, G.N. Aliev, D. Wolverson, J.J. Davies, S.J. Bingham, D.A. Abdulmalik, P.G. Coleman, T. Wang, P.J. Parbrook, *Phys. Status Solidi (c)* 3 (2006) 1919.
- [31] T. Qiu, X.L. Wu, Y.C. Cheng, G.G. Siu, P.K. Chu, *Appl. Phys. Lett.* 88 (2006) 143111.
- [32] Z. Jian, Z. Xiang, W. Yongchang, *Microelectron. Eng.* 77 (2005) 58.
- [33] T. Qiu, X.L. Wu, X. Yang, G.S. Huang, Z.Y. Zhang, *Appl. Phys. Lett.* 84 (2004) 3867.