



Characteristics of GaN-core/Au-shell hetero-nanowires: Effects of thermal annealing on the structural and photoluminescence properties

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ABSTRACT

Keywords:

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GaN-core/Au-shell nanowires were fabricated and the effects of thermal annealing on the structural and photoluminescence (PL) properties were investigated. The surfaces of hetero-nanowires became rough due to the thermal annealing which could be attributed to the agglomeration of Au-shell layers into the cluster-like structures. X-ray diffraction indicated that the thermal annealing enhanced the crystallinity of the Au shell. From Gaussian deconvolution studies, we observed that the Au coating added a green band to the PL spectrum, whereas the thermal annealing enhanced the ultraviolet band. We have discussed the possible emission mechanisms.

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1. Introduction

Since one-dimensional (1D) heterostructures with modulated composition and interfaces are supposed to have diverse functionalities, they are believed to have potential applications in nano-device fabrication [1,2]. Accordingly, many attempts have been made to achieve 1D heterostructures with different material systems, including semiconductor/semiconductor superlattices and metal/insulator nanocables. In spite of their interesting properties and their use in various nanodevice applications, metal/semiconductor nanocables have not been sufficiently studied. This may arise from the difficulty in forming the metal shell layers on semiconductor core nanowires. In this study, we have coated GaN nanowires with Au-shell layers by using the plasma sputtering technique.

Gallium nitride (GaN) nanowires have been the subject of an intense research owing to a variety of potential applications, including blue and ultraviolet light-emitting diodes and laser diodes, high temperature and high power optoelectronic devices, modulators and detectors [3–9]. On the other hand, gold (Au) nanostructures have exhibited novel size-dependent properties that cannot be explained classically [10]. Also, they have many applications such as biological probes [11], submicrometer metallic barcodes [12], surface-enhanced Raman spectroscopy [13,14], plasmon waveguides for optical devices [15], photonic materials [16], and chemical sensors [17].

The Au-shell layer will not only prevent the degradation of core GaN nanowires but also extend the functionalities. The fabrication of nanodevices inevitably comprises a thermal annealing process which will alter/improve the properties of core/shell nanowires. Accordingly, we have investigated the effects of thermal annealing on the structural and optical properties of as-fabricated GaN-core/Au-shell nanowires.

2. Experimental

First, we prepared core GaN nanowires on silver (Ag: about 10 nm)-coated Si substrates and by heating pure GaN powders in a tube furnace. A mixture of Ar (flow rate: 100 sccm) and NH₃ (flow rate: 20 sccm) gases flowed at 1000 °C for 1 h. Second, the substrates were transferred to a turbo sputter coater (Emitech K575X, Emitech Ltd., Ashford, Kent, UK) [18]. By using a circular Au target at room temperature, the sputter time was set to 1 min in high-purity (99.999%) argon (Ar) ambient. During the sputtering process, the DC current was maintained at 65 mA. Subsequently, the GaN-core/Au-shell nanowires were annealed at 600 °C for 10 min in N₂ ambient.

The samples were characterized 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 (EDX). The photoluminescence (PL) measurement was carried out using a 325 nm He-Cd laser. A 55 mW Kimmon laser beam was focused on the sample.

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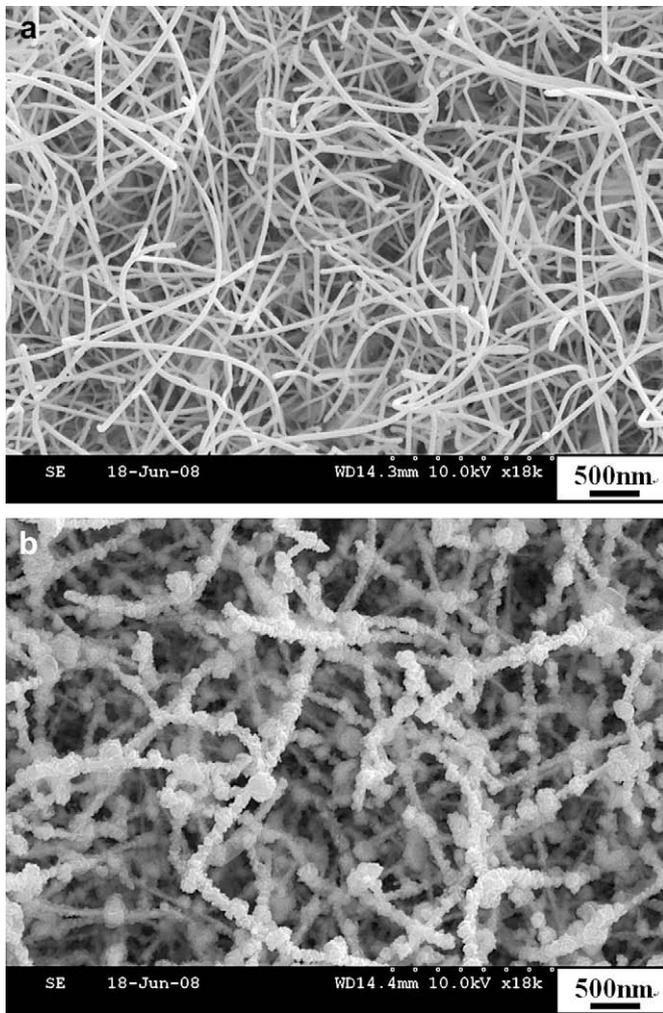


Fig. 1. SEM images of the GaN-core/Au-shell nanowires (a) before and (b) after the thermal annealing.

3. Results and discussion

Fig. 1a and b shows typical SEM images of the GaN-core/Au-shell nanowires before and after thermal annealing, respectively. It is worthwhile to note that the surface of annealed samples appeared more rough-natured than that of as-fabricated ones. Fig. 2a and b shows a TEM image and a corresponding SAED pattern of an as-fabricated GaN-core/Au-shell nanowire, respectively. The SAED pattern can be indexed as the diffraction ring of cubic Au. In a lattice-resolved TEM image shown in Fig. 2c, the space of 0.235 nm between arrowheads corresponds to the distance between two (111) planes of cubic Au, indicating that the nanowire is poly-crystalline. The inset in the upper-left-hand corner of Fig. 2c is the associated EDX spectrum. There are peaks associated with Au, in addition to Ga and N elements in the spectrum.

Fig. 3a shows a TEM image of GaN-core/Au-shell nanowires annealed at 600 °C. By comparing Fig. 3a with Fig. 2a, it was found that Au-shell layers had been transformed to particle-like or cluster-like structures by the thermal annealing. Fig. 3b and c is an EDX spectra from the region indicated by arrow 1 and arrow 2, respectively, in Fig. 3a. Since the region indicated by arrow 2 has a greater portion of blackened area than that by arrow 1, we reveal that the blackened regions in Fig. 3a correspond to the Au-related

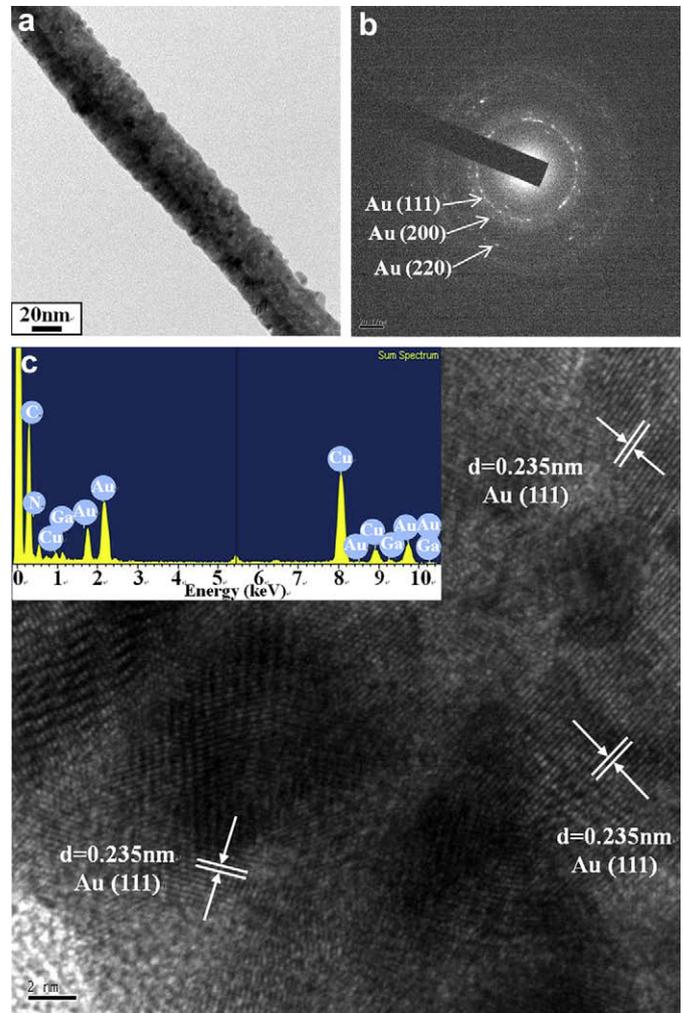


Fig. 2. (a) TEM image of an as-synthesized GaN-core/Au-shell nanowire. (b) Associated SAED pattern image. (c) Lattice-resolved TEM image enlarging an area near the surface of the nanowires in (a). The inset in (c) exhibits an EDX spectrum which confirms the existence of Au elements.

structures. Although the region indicated by arrow 1 also exhibits a cluster-like surface, this may have originated from a very rough GaN surface prior to Au coating. The O content in Fig. 3b was calculated to be about 0.43 atomic %.

Fig. 3d is a lattice-resolved TEM image. In the blackened region, the marked parallel fringes with spacing of 0.235 nm correspond to the (111) plane of cubic Au. Fig. 3e shows the associated SAED pattern, confirming the existence of diffraction rings of cubic Au. By comparing Fig. 3e with Fig. 2b, it can be seen that the SAED pattern became more spotty from thermal annealing. Accordingly, we suggest that the Au shell has become more crystalline as a result of this annealing.

An XRD pattern of core GaN nanowires, shown in Fig. 4a, reveals that the whole spectrum can be indexed in peak position to a crystalline hexagonal wurtzite GaN phase (JCPDS card: No. 02-1078). From the XRD pattern of as-prepared GaN-core/Au-shell nanowires shown in Fig. 4b, it was found that there exists a cubic Au phase (JCPDS card: No. 04-0783), in addition to the GaN phase. Fig. 4c represents an XRD spectrum of annealed GaN-core/Au-shell nanowires. By comparing Fig. 4c with Fig. 4b, we see that the relative intensity of Au-associated peak to GaN-related peaks is increased by thermal annealing at 600 °C. Additionally, from the

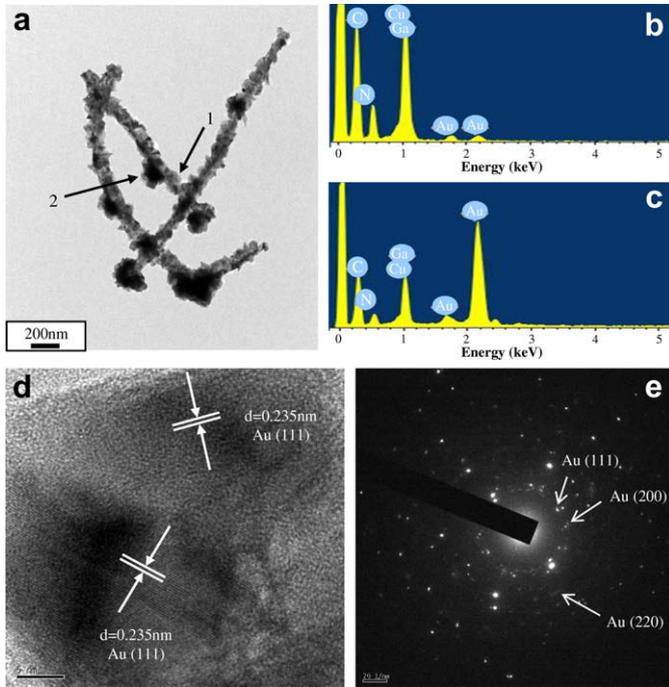


Fig. 3. TEM image of annealed GaN-core/Au-shell nanowires (b,c) EDX spectra from the region indicated by (b) arrow 1 and (c) arrow 2, respectively, in (a). (d) Lattice-resolved TEM image. (e) Corresponding SAED pattern image.

XRD peak broadening analysis, the full-width-at-half-maximum (FWHM) values of the Au-associated peaks are found to decrease by thermal annealing. Thus, the Scherrer formula reveals that the Au grain size becomes larger as a result of the thermal annealing [19]. The result agrees well with the SAED patterns.

Fig. 5a shows a normalized PL spectrum of core GaN nanowires measured at 298 K. The broad emission was divided into three Gaussian functions, which were centred at 2.9 eV in the blue region, 2.4 eV in the green region, and 1.9 eV in the red region, respectively. It is known that the blue light band in GaN is attributed to crystal defects such as $V_{\text{Ga}(\text{Ga vacancy})}$ -related complexes [20,21]. Similarly, the green emission is ascribed to structural defects, including V_{Ga} , $V_{\text{Ga}}\text{-O}_\text{N}$ complexes, etc [22,23]. On the other hand, red emission band in GaN is generally ascribed to vacancy-impurity pairs [24–26], such as a deep donor $V_{\text{N}}\text{C}_\text{N}$ and a deep acceptor $V_{\text{Ga}}\text{O}_\text{N}$ [27,28]. In the present work, we surmise that impurities such as C and O originated from inside the chamber during the high-temperature heating process, inducing the red emission.

Fig. 5b shows a normalized PL spectrum of as-fabricated GaN-core/Au-shell nanowires. In addition to 2.9 eV-centred, 2.4 eV-centred, and 1.9 eV-centred peaks from GaN core nanowires, there exists a green peak at around 2.2 eV. The green emission peak was previously observed from Au whiskers [29] and Au nanorods [30], being related to the interband electronic transition, which is less sensitive to the variation in surrounding temperature [30,31].

Fig. 5c shows a normalized PL spectrum of annealed GaN-core/Au-shell nanowires. This emission can be deconvoluted into five peaks. Being similar to an unannealed sample (Fig. 5b), the PL spectrum has exhibited four peaks, centred at 1.9 eV, 2.2 eV, 2.4 eV, and 2.9 eV, respectively. In addition, it is noteworthy that a relatively strong ultraviolet (UV) emission peak at around 3.2 eV has appeared as a result of thermal annealing. Since XRD spectra revealed that no noticeable compound other than GaN and Au was produced by the annealing, we suggest that the UV emission is

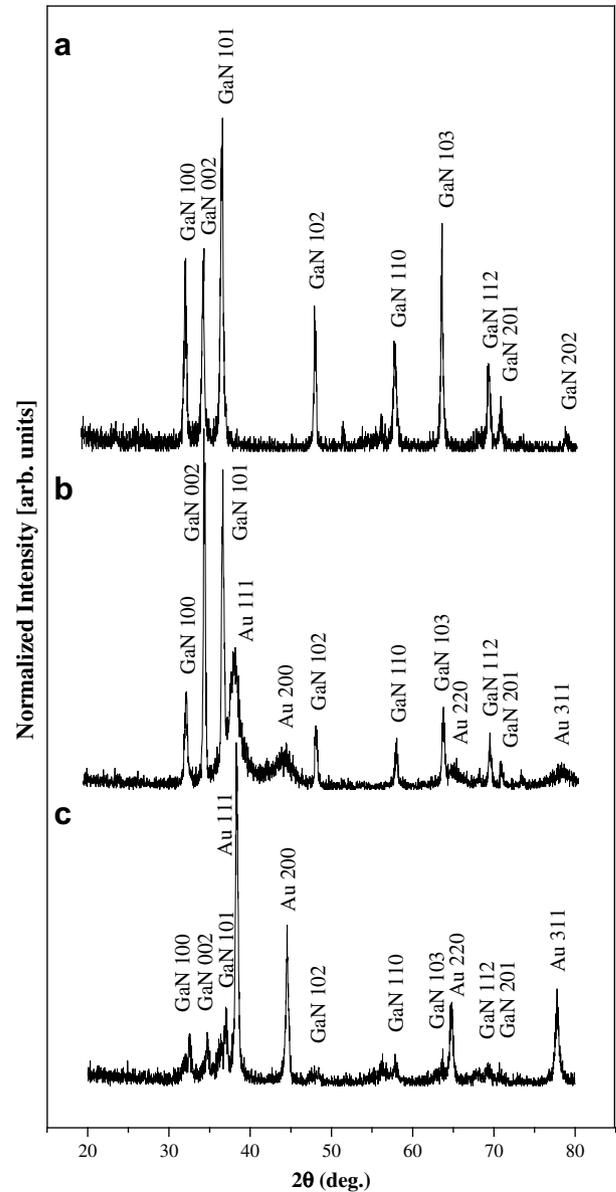


Fig. 4. XRD patterns of (a) core GaN nanowires, (b) unannealed GaN-core/Au-shell nanowires, and (c) annealed GaN-core/Au-shell nanowires.

attributed to a GaN core or Au shell. One possibility is that the UV peak is ascribed to the GaN core nanowires. It is known that the UV emission in GaN is associated with the transition from a shallow donor to a shallow acceptor [23]. Main candidates for the shallow donors are Si_{Ga} and O_N , whereas those for the shallow acceptors are Si_N and C_N [23]. It is surmised that the diffusion of Si from the substrate C and O from inside the chamber will be activated by the thermal annealing at a sufficiently high temperature, ultimately enhancing the UV emission. The other possibility is that the UV peak is attributed to the Au-shell layers. Nevertheless, there has not been any report so far on the UV emission from Au structures, discarding this possibility.

4. Conclusions

In summary, we have fabricated GaN-core/Au-shell nanowires and subsequently investigated the effects of thermal annealing on

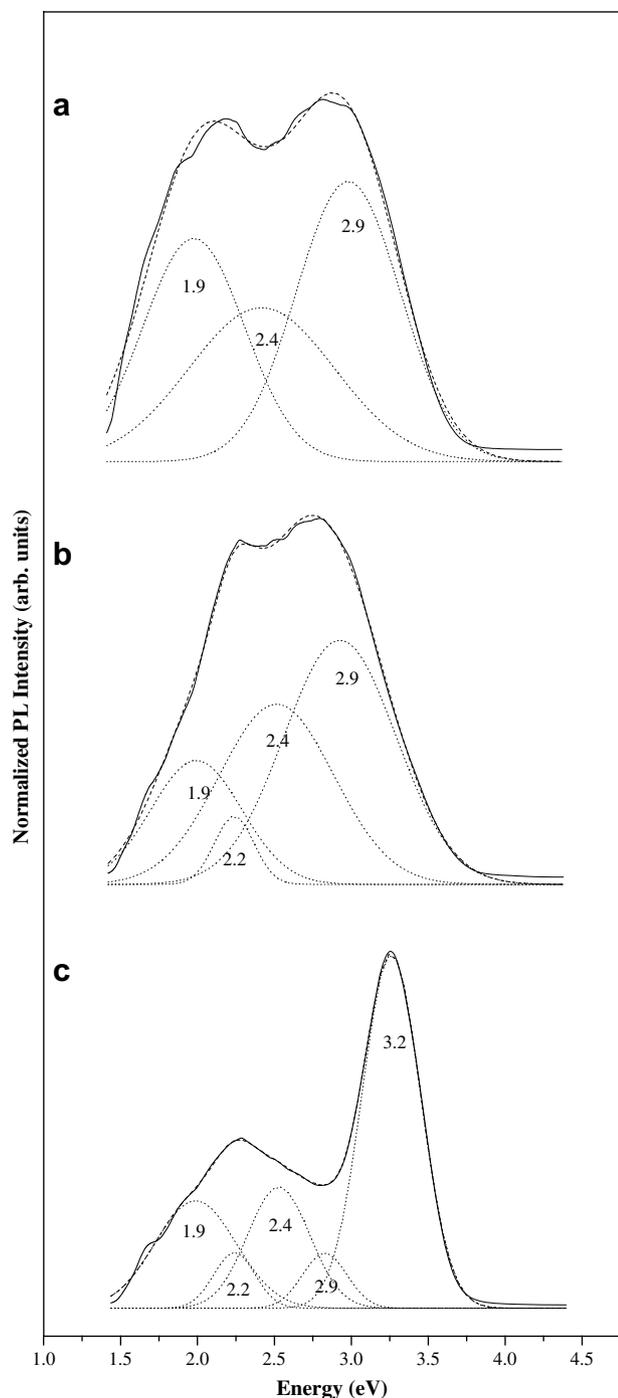


Fig. 5. Normalized PL spectra of (a) core GaN nanowires, (b) Au-coated GaN nanowires prior to thermal annealing, and (c) Au-coated GaN nanowires after thermal annealing.

the structural and optical properties. Thermal annealing has induced morphological and structural changes in the Au-shell layers. Gaussian deconvolution study reveals that the coating of Au has added a green emission band to the PL spectrum of core GaN nanowires, whereas the subsequent thermal annealing at 600 °C has added a UV emission band. It is suggested that the annealing-induced change in PL spectrum resulted from the change in the GaN core nanowires.

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References

- [1] Li Q, Wang C. *J Am Chem Soc* 2003;125:9892.
- [2] Gudixsen MS, Lauhon LJ, Wang J, Smith DC, Lieber CM. *Nature* 2002;415:617.
- [3] Zolper J, Shul R, Baca A, Wilson R, Pearton S, Stall R. *Appl Phys Lett* 1996;68:2273.
- [4] Liu B, Bando Y, Tang C, Xu F, Hu J, Golberg D. *J Phys Chem B* 2005;109:17082.
- [5] Kim HM, Choo YH, Lee H, Kim SI, Ryu SR, Kim DY, et al. *Nano Lett* 2004;4:1059.
- [6] Huang Y, Duan X, Cui Y, Lieber CM. *Nano Lett* 2002;2:101.
- [7] Greytak AB, Barrelet CJ, Li Y, Lieber CM. *Appl Phys Lett* 2005;87:151103.
- [8] Zhong ZH, Qian F, Wang DL, Lieber CM. *Nano Lett* 2003;3:343.
- [9] Sirbuly DJ, Law M, Yan HQ, Yang PD. *J Phys Chem B* 2005;109:15190.
- [10] Wilcoxon JP, Martin JE, Parsapour F, Wiedenman B, Kelley DF. *J Chem Phys* 1998;108:9137.
- [11] Taton TA, Mirkin CA, Letsinger RL. *Science* 2000;289:1757.
- [12] Nicewarner-Peña SR, Freeman RG, Reiss BD, He L, Peña DJ, Walton ID, et al. *Science* 2001;294:137.
- [13] Dick LA, McFarland AD, Haynes CL, Van Duyne RP. *J Phys Chem B* 2002;106:853.
- [14] Tessier PM, Velev OD, Kalambur AT, Rabolt JF, Lenhoff AM, Kaler EW. *J Am Chem Soc* 2000;122:9554.
- [15] Maier SA, Brongersma ML, Kik PG, Meltzer S, Requicha AAG, Atwater HA. *Adv Mater* 2001;13:1501.
- [16] Hayward RC, Saville DA, Aksay IA. *Nature* 2000;404:56.
- [17] Aherne D, Rao SN, Fitzmaurice D. *J Phys Chem B* 1999;103:1821.
- [18] Kim HW, Shim SH, Lee JW. *Carbon* 2007;45:2695.
- [19] Cullity BD. *Elements of X-ray diffraction*. Addison-Wesley; 1978.
- [20] Reshchikov MA, Korotkov RY. *Phys Rev B* 2001;64:115205.
- [21] Yang HC, Lin TY, Chen YF. *Phys Rev B* 2000;62:12593.
- [22] Reshchikov MA, Morkoc H, Park SS, Lee KY. *Appl Phys Lett* 2001;78:3041.
- [23] Reshchikov MA, Morkoc H. *J Appl Phys* 2005;97:061301.
- [24] Nakamura S, Iwasa N, Senoh M, Mukai T. *Jpn J Appl Phys* 1992;31:1258.
- [25] Kaufmann U, Kunzer M, Obloh H, Maier M, ChManzRamakrishnan A, Santic B. *Phys Rev B* 1999;59:5561.
- [26] Hofmann DM, Meyer BK, Alves H, Leiter F, Burkhard W, Romanov N, et al. *Phys Stat Sol A* 2000;180:261.
- [27] Wang L, Richter E, Weyers M. *Phys Stat Sol A* 2007;204:846.
- [28] Zeng S, Aliev GN, Wolverson D, Davies JJ, Bingham SJ, Abdulmalik DA, et al. *Phys Stat Sol C* 2006;3:1919.
- [29] Qiu T, Wu XL, Siu GG, Chu PK. *Appl Phys Lett* 2005;87:223115.
- [30] Mohamed MB, Volkov V, Link S, El-Sayed MA. *Chem Phys Lett* 2000;317:517.
- [31] Mooradian A. *Phys Rev Lett* 1969;22:185.