Photoluminescence characteristics of GaAsSbN/GaAs epilayers lattice-matched to GaAs substrates

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Abstract

The photoluminescence (PL) characteristics of GaAsSbN/GaAs epilayers grown by molecular beam epitaxy (MBE) are carefully investigated. The results show that antimony (Sb) incorporation into GaNAs material has less influence on the N-induced localization states. For the same N concentration, GaAsSbN material can reach an emission wavelength near 1.3 μm more easily than GaInNAs material. The rapid thermal annealing (RTA) experiment shows that the annealing induced rearrangement of atoms and related blueshift in GaAsSbN epilayers are smaller than those in GaNAs and GaInNAs epilayers. The GaAsSbN material can keep a longer emission wavelength near 1.3 μm-emission even after the annealing treatment. Raman spectroscopy analysis gives further insight into the structure stability of GaAsSbN material after annealing.
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1. Introduction

The nitride III–V semiconductors alloys such as GaNAs and GaInNAs have attracted a lot of attentions in recent past owing to their unique physical properties and potential applications for achieving the technologically important telecommunication wavelengths of 1.3 or 1.55 μm with GaAs-based materials [1–3]. In addition, the fabrications of GaInNAs- and GaNAs-related vertical cavity emitting sources on GaAs substrates can be benefited from the good characteristics of GaAs/AlAs Bragg mirrors [4]. To achieve the emission wavelength beyond 1.3 μm, so many N atoms are necessarily incorporated into the Ga(In)As alloy that it is difficult to obtain a high crystal quality of such

materials [5]. In order to guarantee the performance of 1.3–1.55 μm Ga(In)NAs/GaAs QW lasers, the N composition incorporated into the Ga(In)NAs well should be considerably small. The most promising range of N composition is also about 0–2%, commonly no more than 1% [6]. Many methods were proposed to get longer emission wavelength with lower N incorporation, e.g. changing the barrier material to reduce the barrier height and adding a little Sb to GaInNAs quantum wells to form GaInNAs:Sb alloy [7,8]. Recently, a new alternative alloy, GaAsSbN, proposed by J.C. Harmand et al. offers another possibility to get longer wavelength with lower N concentration compared with GaInNAs [9,10]. Another advantage of GaAsSbN alloy is: it cannot only offer the possibility of simultaneous reducing of the band-gap and maintaining the lattice parameter of alloy like GaInNAs, but also provide the possibility of independently tuning the conduction band and the valence band offsets in devices for band gap engineer and device

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structures [11]. Besides that, the characteristics and the preparation of quaternary GaAsSbN are simpler than those of quinary GaInNAs:Sb. According to the previous reports, the MBE growth, the PL properties and annealing processing of the GaAsSbN QWs system have been investigated focused on obtaining high quality QWs for semiconductor laser devices [11–13]. However, more research works on the fundamental optical and structure properties of GaAsSbN alloy are still needed.

In this article, the detailed investigations on the PL properties of GaAsSbN/GaAs epilayer grown by MBE are reported with two reference samples of GaInNAs and GaNAs epilayers. Raman scattering and rapid thermal annealing (RTA) techniques are applied to GaAsSbN epilayer to investigate the structural properties of local bonding of N atoms in GaAsSbN.

2. Experimental details

The GaAsSbN/GaAs epilayer and two reference samples of GaInNAs/GaAs and GaNAs/GaAs were grown under the same condition by MBE. The thickness of GaAsSbN, GaInNAs, and GaNAs epilayers are all 1 μm. The N concentration of all the three samples is 2%, and the concentration of In and Sb in samples GaInNAs and GaAsSbN are 5 and 8%, respectively, which is almost lattice matched to the underlying GaAs substrate. Rapid thermal annealing (RTA) was carried out in a flowing N_2 gas ambient on these samples covered with a protective GaAs wafer in a homemade RTP-300 rapid thermal processor. The PL signal was collected by a Nicolet FTIR760 Fourier spectrometer and detected by a cooled Ge detector with a 514.5 nm excitation of an Ar-ion laser. The sample temperature was controlled by a variable-temperature (10–300 K) close-cycle cryostat. The Raman spectra were recorded by the Dilor Super Labram with a typical resolution of $1.0\ cm^{-1}$ in a back-scattering geometry at room temperature. The laser excitation is 632.8 nm line of a He–Ne laser.

3. Results and discussions

Fig. 1 shows the room temperature PL spectra of GaAsSbN epilayer along with GaInNAs and GaNAs reference epilayers. The emission wavelength of GaAsSbN system extends up to 1.32 μm, and those of GaInNAs and GaNAs epilayers with the same N concentration are only 1.17 and 1.13 μm, respectively. For the GaNAs material, the 2% N concentration can induce a PL energy redshift of 323 meV to the band gap of bulk GaAs, which corresponds to ∼160 meV per percentage of N. The PL energy shifts of the studied GaInNAs and GaAsSbN samples are 363 and 482 meV away from the band gap of GaAs, respectively. If one assumes an independent change of the band gaps of
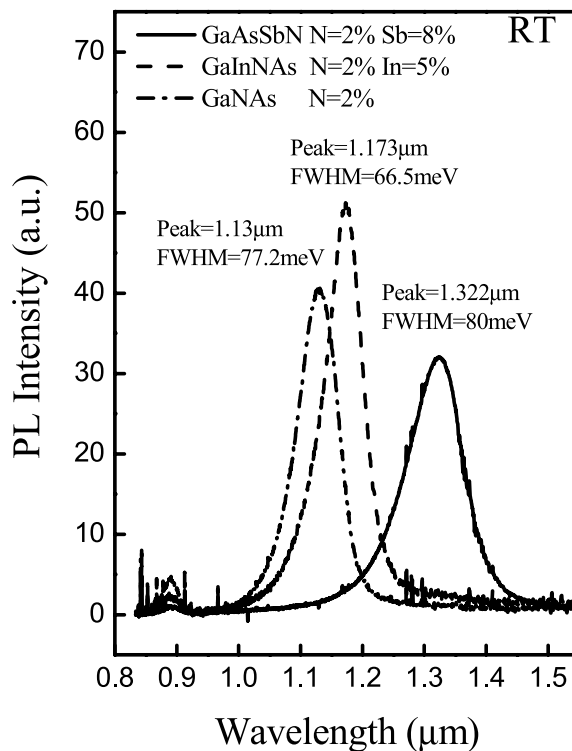

Fig. 1. Room temperature PL spectra of GaAsSbN, GaInNAs and GaNAs with the same N composition.

three materials by In, Sb and N and a linear change of their band gaps caused by In and Sb incorporation, we can get an 8 meV energy decrease per In percent incorporation and a 20 meV energy decrease per Sb percent incorporation. Therefore, with the same incorporated composition, GaAsSbN material will achieve a long emission wavelength beyond 1.3 μm much easily than Ga(In)NAs materials. On the other hand, compared with GaNAs, the full width of half maximum (FWHM) of GaInNAs is narrower and the PL intensity increases due to the introduction of In, a fact consisting with our previous results [14]. In opposition to the GaInNAs, the FWHM of GaAsSbN is slightly broader and the PL intensity decreases due to the introduction of Sb. The optical quality of GaAsSbN epilayer can be improved effectively by RTA, which will be shown later.

The temperature dependent PL spectra of sample GaAsSbN are measured under different excitation intensities, and those under relatively high excitation intensity (5 W/cm²) are depicted in Fig. 2(a). Those PL spectra of GaAsSbN are dominated by the peaks originated from near-band-edge transition, and only one PL peak was observed in the whole temperature range whose PL peak energy shows a monotonously decrease with the increase in temperature. This behavior can be well fitted by an empirical relation which was established for the band-gap-like energy dependence on the temperature [15], as shown in Fig. 2(b). The temperature-dependent PL peak of the reference
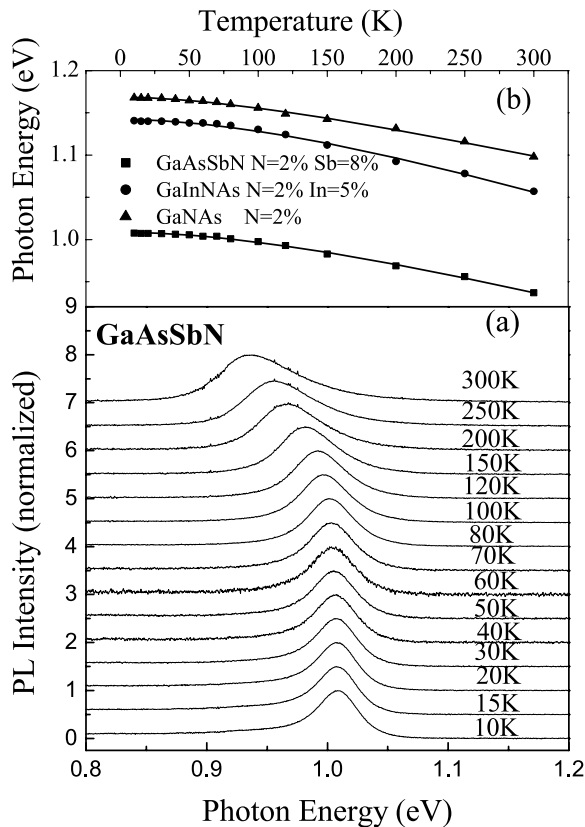
Fig. 2. (a) PL spectra of GaAsSbN varied from 10 to 300 K under excitation power 5 W/cm^2. (b) Temperature dependence of the PL peak energy of GaAsSbN, GaInNAs, and GaNAs. The continuous lines are fitted according to Varshni equation.

Fig. 3. (a) PL spectra of GaAsSbN varied from 10 to 300 K under excitation power 0.5 W/cm^2. (b) Temperature dependence and FWHM of the PL peak energy of GaAsSbN, GaInNAs, and GaNAs.

samples of GaInNAs and GaNAs material are also shown in Fig. 2(b). When the excitation intensity is decreased to about 0.5 W/cm^2, the PL peak energy of the GaAsSbN epilayer displays an anomalous temperature behavior in the range of 10–300 K, as shown in Fig. 3(a). With the increase in temperature, the dominant PL peak first redshifts from 10 to 30 K, then blueshifts from 30 to 80 K, and redshifts again above 80 K, as shown by the dot-dashed line in Fig. 3(a). The very similar S-shape temperature behavior was also reported in GaInNAs and GaNAs systems, which was attributed to the N-related localization states induced by the alloy potential fluctuation [16–18]. Fig. 3(b) shows the peak energy and FWHM of the PL peak of GaAsSbN system as a function of temperature denoted by solid and hollow dots, respectively. The temperature dependences of PL peak energy and FWHM of the reference GaInNAs and GaNAs samples measured under the same conditions are also shown in Fig. 3(b) for comparison. All three samples show a very similar behavior of the anomalous temperature dependence of the PL peak energy and FWHM. According to the analysis in Ref. [27], the S-shape temperature behavior induced by nitrogen-induced bound states can be well
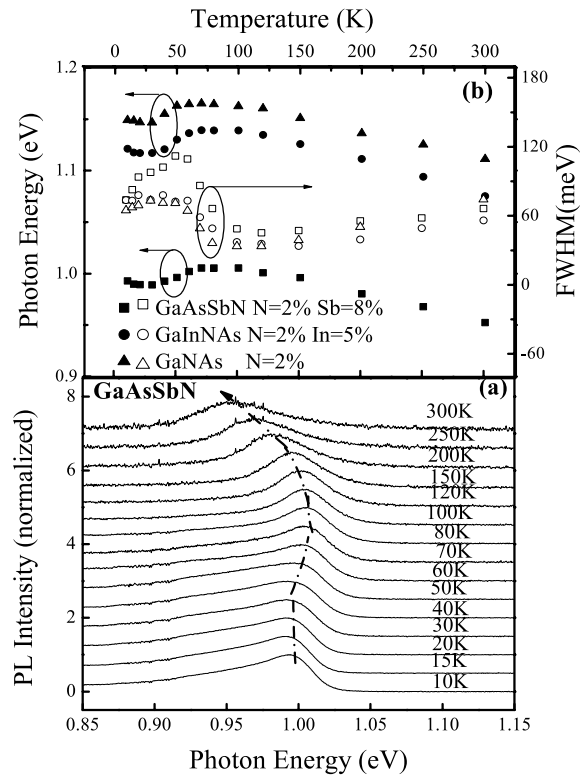
discerned only at lower excitation power density. So we can suggest that the anomalous temperature behavior is mainly determined by the incorporation of N atoms, and less affected by the additional introduction of In or Sb atoms.

Fig. 4(a)–(c) shows the room temperature PL spectra of three as-grown and annealed samples. In addition, the PL spectra of as-grown and annealed GaAsSbN samples at 10 K are shown in Fig. 4(d). The PL intensities of three samples all increase after annealing treatment, whether at 10 K or at room temperature. The FWHM of the PL peak of GaAsSbN epilayer reduces markedly from 69 to 38 meV at 10 K. It indicates that the optical quality of GaAsSbN sample is well improved by the RTA treatment. The annealing-induced blueshift of GaNAs and GaInNAs materials at room temperature are 19 and 33 meV, respectively, however, GaAsSbN system exhibits a much smaller annealing-induced blueshift of 1.5 meV. The annealing-induced blueshift in GaAsSbN system at 10 K is also considerably small, only 9 meV, as shown in Fig. 4(d).

The PL peak of Ga(In)NAs QWs system exhibits a considerable blueshift after the RTA treatment because of the interdiffusion across the hetero-interface and the possible reorganization related to the In–N interaction assisted by the point-defect [7,20,21]. For the present case, the N–As interdiffusion can be neglected for those
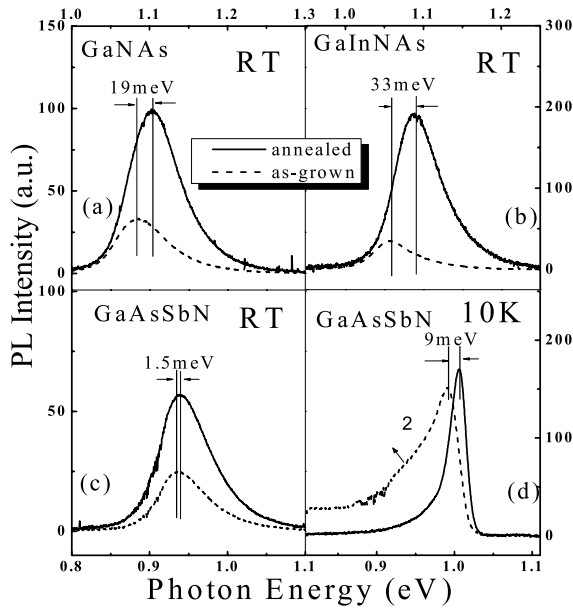
Fig. 4. (a)–(c) are the room temperature PL spectra of GaNAs, GaInNAs and GaAsSbN before and after annealing, respectively, and (d) is the PL spectra of GaAsSbN measured at 10 K before and after annealing.

epilayer samples according to many results of TEM measurements [11,26]. Therefore, the difference of the post-annealing effect on the PL properties between GaAsSbN and Ga(In)NAs systems might be related with the structure change of material. For GaNAs system, the N atoms reorganization assisted by the point-defect during annealing process is the main reason for blueshift [19,22,23]. The larger blueshift appeared in GaInNAs system than in GaNAs system is due to the additional effect induced by the existent of In atoms in annealing process, such as the In–N interaction or the formation of N–In bonds due to the Ga site around N atom replaced by In atom through the point-defect assisted reorganization in the annealing process [24]. Similar to GaInNAs system, short-range atomic rearrangements are indeed also expected to minimize the local strain around N or Sb sites in GaAsSbN system. But only one group III element (Ga) existed in GaAsSbN system, and the N can only be bonded to the Ga. In addition, the N and Sb are all group V atoms, they are the second neighbor atoms in the lattice structure. So the effect of Sb–N interaction or the substitute of Ga around N atom by Sb through the point-defect-assisted reorganization to reduce the local strain should weaken. Therefore, the electronic structure of GaAsSbN system would be less sensitive to the thermal treatment than that of GaInNAs system. Meantime, the existing of Sb reduces the local strain around N atoms of as-grown samples compared with GaNAs system, which would make the N clustering effect weaker. As a consequence, the

annealing-induced blueshift in GaAsSbN system will be smaller than that in GaInNAs and GaNAs systems.

Raman spectroscopy is an effective method to measure the change in the local bonding surrounded the N atoms [25]. Fig. 5 shows the Raman spectra of the as-grown 1 μm-thick GaAsSbN epilayer and that annealed at 700 °C for 60 s. Raman spectra were excited by a red 632.8 nm laser, whose photon energy (1.96 eV) is near resonant with the E_+ gap of GaAsSbN materials. The as-grown sample exhibits three Raman bands: GaAs-like TO_1 at 268 cm^{-1}, GaAs-like LO_1 at 290 cm^{-1}, and GaN-like LO_2 mode at 468 cm^{-1}. The observation of the forbidden TO phonon mode at 268 cm^{-1} is mainly due to alloy disorder in the sample. The incorporation of Sb in GaAsSbN epilayer will reduce the effective force constant of Ga–N bonds in GaAsSbN alloy and the local strain around N atoms. This can result in the frequency of the GaN-like mode in GaAsSbN epilayer is considerably lower than that (476 cm^{-1}) of GaAsN alloy with the same N composition. For the annealed sample, its Raman spectrum is nearly the same as that of as-grown sample, such as the mode frequency of the GaN-like phonon mode, and the relative intensities of the GaN-like LO_2 and the GaAs-like TO modes with respect to that of the LO phonon strengthens. It indicates that the local bonding surrounded the N atom is less changed during the annealing process, as discussed above.
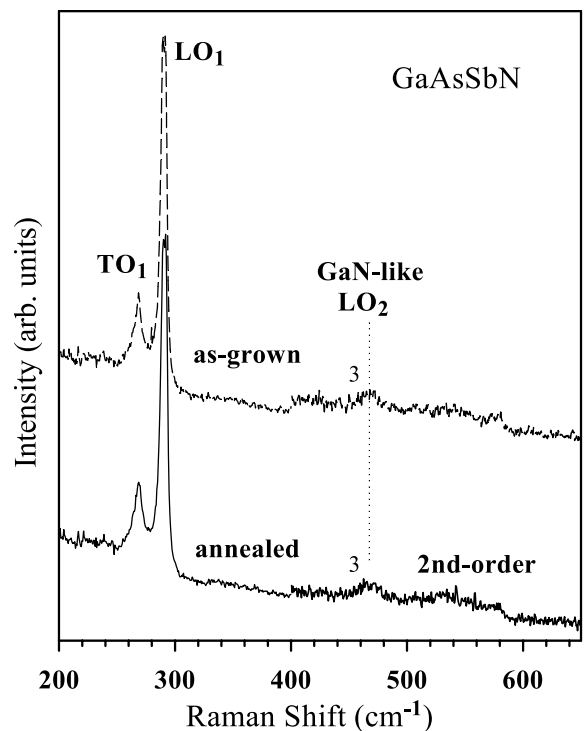

Fig. 5. Raman spectra of GaAsSbN before and after annealing under the incident photon energy of 1.96 eV.

4. Conclusion

GaAsSbN alloy is presented as a potential candidate to fabricate long wavelength telecommunication sources on GaAs substrates. The fundamental optical and structure properties of GaAsSbN alloys are carefully investigated by means of the photoluminescence spectra of GaAsSbN/GaAs epilayer grown by MBE. Compared with GaInNAs material, it is easier to achieve longer wavelength with the lattice almost matched to the underlying GaAs. The temperature-dependent PL spectra show that the N-induced localization states in the GaAsSbN system are only decided by the incorporation of N atoms and less influenced by the additional incorporation of Sb or In atoms. RTA can effectively improve the optical properties of GaAsSbN alloys, and the GaAsSbN epilayer is less sensitive to the thermal treatment due to the fact that the Sb atom is the same group V atom as N and is the second nearest neighboring to N atom in GaAsSbN system. Hence the annealing induced rearrangement of atoms and the related blueshift in the GaAsSbN epilayer will be smaller than those in the GaNAs and GaInNAs samples. The GaAsSbN epilayer can keep a longer emission wavelength near 1.3 μm-emission wavelength even after annealing treatment. Raman spectroscopy analysis of GaAsSbN indicates that the local bonding surrounding the N atom is changed little during the annealing process.

Acknowledgements

References

[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Wataniki, Y. Yazama, Jpn. J. Appl. Phys. 35 (1996) L1273.

[2] T. Kitatani, K. Nakahara, M. Kondow, K. Uomi, T. Kitatani, Jpn. J. Appl. Phys. 39 (2000) L86.

[3] S.R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J. Banas, B.E. Hammons, Appl. Phys. Lett. 74 (1999) 729.

[4] K.D. Choquette, J.E. Klem, A.J. Fischer, O. Blum, A.A. Allerman, I.J. Fritz, S.R. Kurtz, W.G. Breiland, R. Sieg, K.M. Geib, J.W. Scott, R.L. Naone, Electron. Lett. 36 (2000) 1388.

[5] L.F. Bian, D.S. Jiang, S.L. Lu, J. Cryst. Growth 253 (2003) 155.

[6] M. Fischer, M. Reinhardt, A. Forchelm, Electron. Lett. 36 (2000) 1208.

[7] L.F. Bian, D.S. Jiang, S.L. Lu, J.S. Huang, K. Chang, L.H. Li, J.C. Harmand, J. Cryst. Growth 250 (2003) 339.

[8] X. Yang, J.B. Heroux, L.F. Mei, W.I. Wang, Appl. Phys. Lett. 78 (2001) 4068.

[9] G. Ungaro, Le Roux, R. Teissier, J.C. Harmand, Electron. Lett. 35 (1999) 15.

[10] J.W. Ager III, W. Walukiewicz, Semicond. Sci. Technol. 17 (2002) 741.

[11] J.C. Harmand, G. Ungaro, J. Ramos, E.V.K. Rao, G. Saint-Girons, R. Teissier, G. Le Roux, L. Largeau, G. Patriarche, J. Cryst. Growth 227–228 (2001) 553.

[12] S.A. Lourenco, I.F.L. Dias, L.C. Pocas, J.L. Duzrte, J.B.B. de Oliveira, J.C. Harmand, J. Appl. Lett. 93 (2003) 4475.

[13] J.C. Harmand, G. Ungaro, L. Largeau, G. Le Roux, Appl. Phys. Lett. 77 (2000) 2482.

[14] B.Q. Sun, D.S. Jiang, Z. Pan, L.H. Li, H. Wu, Appl. Phys. Lett. 77 (2000) 4148.

[15] Y.P. Varshni, Physica (Utrecht) 34 (1967) 149.

[16] L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vannuffel, A. Million, A. Chenevas-Paule, Appl. Phys. Lett. 76 (2000) 2241.

[17] S. Francoeur, S.A. Nikishin, C. Jin, Y. Qiu, H. Temkin, Appl. Phys. Lett. 75 (1999) 1538.

[18] P.R.C. Kent, Alex Zunger, Appl. Phys. Lett. 79 (2001) 1977.

[19] U. Tisch, E. Finkman, J. Salzman, Appl. Phys. Lett. 81 (2002) 463.

[20] E-M. Paveleescu, T. Jouhti, M. Dumitrrescu, P.J. Klar, S. Karirinne, Y. Fedorenko, M. Pessa, Appl. Phys. Lett. 83 (2003) 1497.

[21] Wei Li, M. Pessa, T. Ahlgren, J. Decker, Appl. Phys. Lett. 79 (2001) 1094.

[22] I.A. Buyanova, G. Pozina, P.N. Hai, N.Q. Thinh, J.P. Bergman, W.M. Chen, H.P. Xin, C.W. Tu, Appl. Phys. Lett. 77 (2000) 2325.

[23] Z. Pan, L.H. Li, Y.W. Lin, B.Q. Sun, D.S. Jiang, W.K. Ge, Appl. Phys. Lett. 78 (2001) 2217.

[24] J.C. Harmand, A. Caliman, E.V.K. Rao, L. Largeau, J. Ramos, R. Teissier, L. Travers, G. Ungaro, B. Theys, I.F.L. Dias, Semicond. Sci. Technol. 17 (2002) 778.

[25] J. Wagner, T. Geppert, K. Köhler, P. Ganser, N. Herres, J. Appl. Lett. 90 (2001) 5027.

[26] E. Tournié, M-A. Pinault, M. Laügt, J.-M. Chauveau, A. Trampert, K.H. Ploog, Appl. Phys. Lett. 82 (2003) 1845.

[27] X.G. Liang, D.S. Jiang, L.F. Bian, Z. Pan, L.H. Li, R.H. Wu, Chin. Phys. Lett. 19 (2002) 1203.