



Influence of thermal annealing duration of buffer layer on the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ grown on InP substrate by LP-MOCVD

Xia Liu^{a,b}, Hang Song^{a,*}, Guoqing Miao^a, Hong Jiang^a, Lianzhen Cao^{a,b}, Dabing Li^a, Xiaojuan Sun^a, Yiren Chen^a

^a Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:

Received 6 August 2010

Received in revised form

16 September 2010

Accepted 16 September 2010

Available online 13 October 2010

Keywords:

$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$

MOCVD

Buffer layer annealing duration

Crystalline quality

ABSTRACT

$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers were grown on InP substrates using a two-step growth technique by LP-MOCVD. A homogeneous low-temperature (450 °C) $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layer was introduced to improve the crystalline quality of epilayers. The influence of low-temperature buffer layer deposition condition, such as thermal annealing duration, on the crystalline quality of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer was investigated. Double-crystal X-ray diffraction measurement, Hall measurement, and Raman scattering spectrum were used to evaluate the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. Atomic force microscope was used to study the surface morphology. It is found that the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer, with buffer layer thermal annealing for 5 min, exhibits the best crystalline quality. The change of the surface morphology of the buffer layer after thermal annealing treatment was suggested to explain the phenomenon.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The ternary semiconductors $\text{In}_x\text{Ga}_{1-x}\text{As}$ have numerous applications because of the range of band gaps (0.35–1.43 eV) available over the composition range. The growth of high In content $\text{In}_x\text{Ga}_{1-x}\text{As}$ epilayers on lattice-mismatched InP substrates has attracted much attention due to the potential applications in the field of infrared detectors, spectral imaging, gas sensors, and spectroscopy [1–3]. However, direct growth of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ films on InP substrate exhibit poor quality due to the large mismatch of lattice constant between $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ and InP. Many schemes [4–7] have been developed to solve this problem, in which two-step growth technique was an effective and convenient way [8]. In two-step growth method, the low-temperature buffer layer is an important issue and an actively investigated subject. The deposition conditions of buffer layer, such as buffer layer thickness [9] and buffer growth temperature [10] on properties of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers by the two-step growth methods have been reported. Even if low-temperature growth of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer is available, annealing treatment is necessary to improve its quality. Thermal annealing is one of the most common methods to reduce the defects and improve the quality of as-grown epilayers. In particular, thermal annealing temperature and duration are the most effective

factors to improve the epilayer's quality. However, there are hardly any reports about the thermal annealing duration of buffer layer on the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers.

In this paper, we studied the influence of buffer layer thermal annealing duration on the properties of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers grown on InP substrate by low pressure metalorganic chemical vapor deposition (LP-MOCVD). To more efficiently improve the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers, a homogeneous buffer layer was used and thermal annealing for various durations. Using the optimum buffer layer, high quality $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ was obtained. The reason of the annealing durations on the quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers was also discussed.

2. Experimental procedure

$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers were grown on Fe-doped InP (100) substrates at 70 Torr by MOCVD in a horizontal reactor. Trimethyl-indium (TMIn), Trimethyl-gallium (TMGa) and arsine (AsH_3) diluted to 10% were used as source materials, respectively. The hydrogen (H_2) is used as carrier gas.

$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer growth was carried out by the following processes. Firstly, InP substrates were thermally cleaned in a PH_3 gas at 630 °C for 10 min to eliminate the oxides of the surface. Secondly, a low-temperature $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layer was deposited on InP substrate at 450 °C with the thickness of 100 nm to act as a template for succeeding epilayers and accommodate lattice strain caused by both lattice mismatch and thermal one.

* Corresponding author. Tel.: +86 431 8462 7073; fax: +86 431 8462 7073.

E-mail address: songh@ciomp.ac.cn (H. Song).

Table 1
FWHM of the double-crystal X-ray rocking curves of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers at various thermal annealing temperatures.

Annealing temperature (°C)	Annealing duration (min)	FWHM of DCXRD (arcsec)
510	10	1200.0
530	10	1080.0
550	10	1620.0
580	10	2028.1
630	10	2235.2

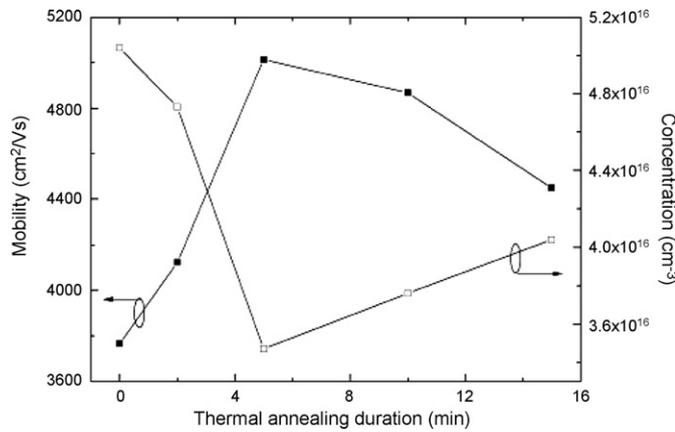


Fig. 1. The Hall mobility and carrier concentration measured at room temperature as a function of the buffer layer thermal annealing duration.

Thirdly, the buffer layer was in-situ thermal annealing for various durations in AsH_3 ambient. The effect of thermal annealing temperature of buffer layer on crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers has been investigated by FWHM of DCXRD in our work and the results of DCXRD are shown in Table 1. It is obvious that the buffer layer thermal annealing temperature was chosen 530°C . Finally, the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer was grown on the annealed buffer layer at 530°C . The thickness of the epilayer is about $1.4\ \mu\text{m}$. The growth of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers is kept under the same conditions, but the buffer annealing conditions is different for samples. The annealing duration was selected 0, 2, 5, 10, and 15 min and the samples were named as A_1 , A_2 , A_3 , A_4 , and A_5 , respectively.

Double-crystal X-ray diffraction (DCXRD, Bruker D8) is performed to obtain the rocking curves of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. Rocking curves were taken for the symmetric (004) reflections. Hall measurement (Lakeshore 7707) was obtained using Van der Pauw technique at room temperature. The Raman scatter spectrum (LabRam Infinity) was measured at room temperature in backscattering geometry using the 488 nm line of an Ar^+ laser as the excitation source. The atomic force microscope (AFM, Veeco multi-mode) was used to study the surface morphology of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layers.

Table 2
Thermal annealing parameters, FWHM of the double-crystal X-ray diffractions and the dislocation density of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers.

Sample no.	Annealing temp. (°C)	Annealing duration (min)	FWHM (arcsec)	Estimated dislocation density ($\times 10^9\ \text{cm}^{-2}$)
A_1	530	0	2349.6	8.05
A_2	530	2	1781.5	4.63
A_3	530	5	1060.0	1.64
A_4	530	10	1080.0	1.70
A_5	530	15	1382.3	2.79

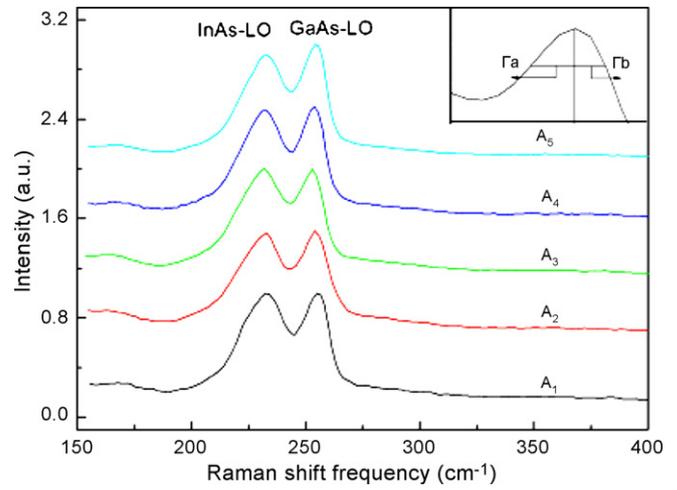


Fig. 2. Raman spectrum of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer with buffer layer thermal annealing for 0, 2, 5, 10, and 15 min, respectively. The inset shows Γ_a and Γ_b which is used in asymmetry ratio (Γ_a/Γ_b) of Raman scattering spectra.

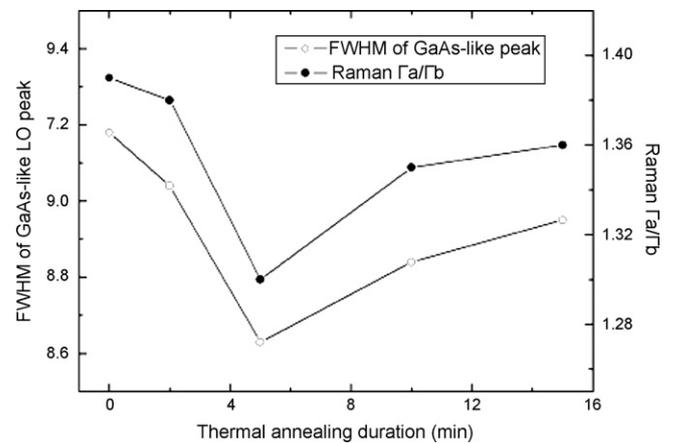


Fig. 3. The FWHM of GaAs-like LO peak and asymmetry ratio (Γ_a/Γ_b) of samples A_1 , A_2 , A_3 , A_4 and A_5 with different thermal annealing duration of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers.

3. Results and discussion

The influence of buffer layer thermal annealing duration on crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer was studied by DCXRD measurement. The full-width at half-maximum (FWHM) value of the DC-rocking Curve with different thermal annealing durations was shown in Table 2. We observed that the value of FWHM strongly depends on the thermal annealing duration. It is known that the upper limit threading dislocation density can be estimated from the FWHM of (004) DCXRD signal using the formula [11]:

$$N_{\text{dis}} = \frac{(\text{FWHM})^2}{9b^2} \quad (1)$$

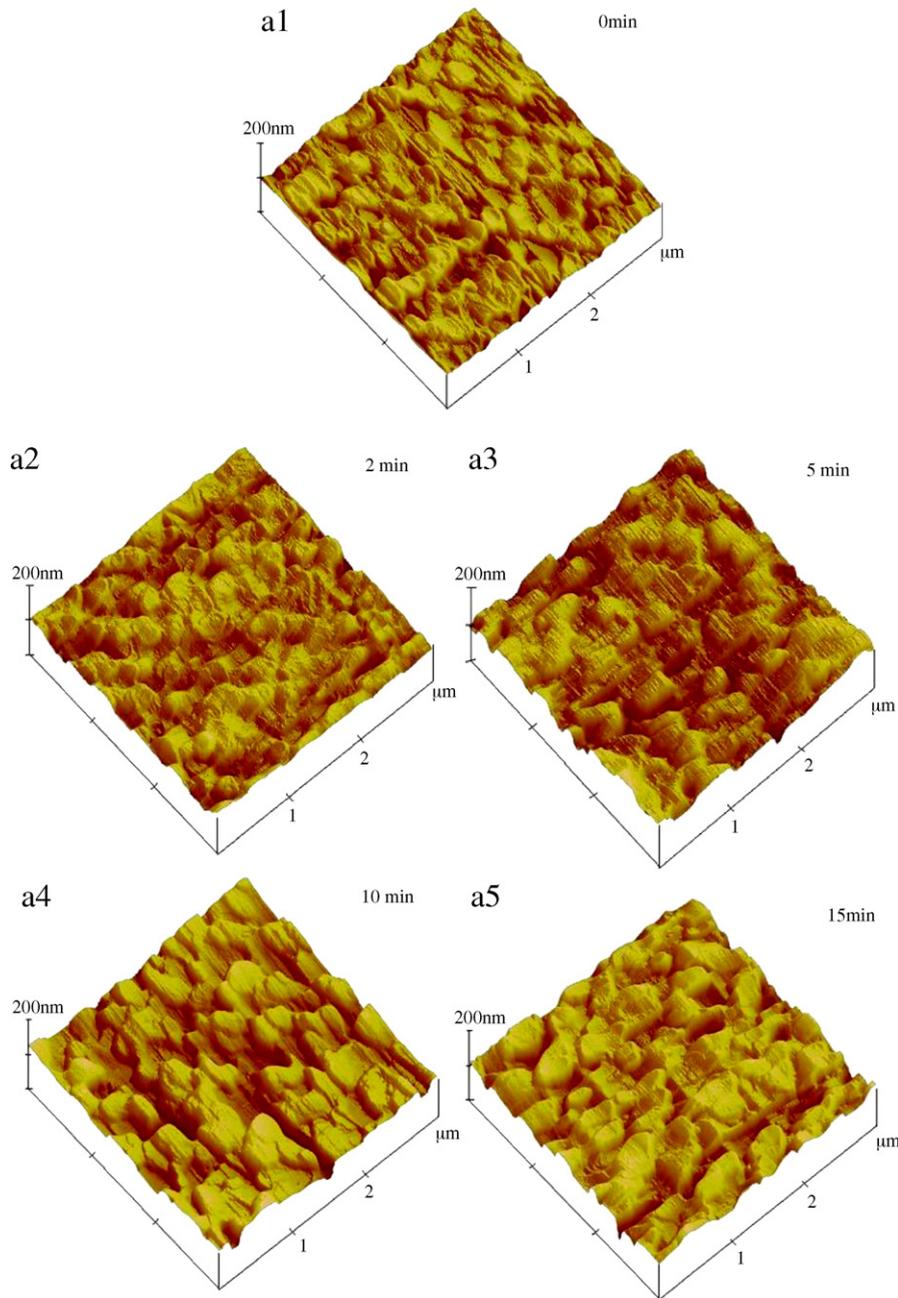


Fig. 4. AFM images of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layers over an area ($3 \times 3 \mu\text{m}^2$): (a1) as-grown, (a2) thermal annealing for 2 min, (a3) thermal annealing for 5 min, (a4) thermal annealing for 10 min, and (a5) thermal annealing for 15 min.

where FWHM is in radians, b is the length of the Burgers vector of the dislocations, and N_{dis} is the density of dislocations (cm^{-2}). The estimated dislocation density was also displayed in Table 2. Therefore, the FWHM value can be used to evaluate the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. It is found that the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer with buffer layer thermal annealing for 5 min has the minimum dislocation density and the best crystalline quality. It indicates that the changes of the FWHM of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer were related to the thermal annealing duration of buffer layers. It is found that the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer can be improved by optimizing the thermal annealing duration of buffer layers.

The carrier concentration and the electron mobility are measured at room temperature and used to further characterize the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. Fig. 1 shows Hall mobility and carrier concentration versus the buffer layer thermal

annealing duration at room temperature. It clearly shows that the buffer layer thermal annealing duration has strong influence on the carrier concentrations and mobility of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. The lowest carrier concentration and highest mobility measured at room temperature is $3.47 \times 10^{16} \text{ cm}^{-3}$ and $5013.5 \text{ cm}^2/\text{Vs}$, which occur at buffer layer thermal annealing duration of 5 min. In the epilayers, the residual misfit dislocations that act as scattering center can reduce the carrier mobility. Hereby, the density of misfit dislocations in the epilayer of sample A_3 is the least. This result indicates that the thermal annealing process does reduce the dislocation concentration of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epitaxial layers. That is, the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer has the best electron properties when the buffer layer was thermal annealing for 5 min.

Raman scattering [12] is an indirect way to characterize the crystalline quality of materials. Fig. 2 shows the Raman scattering spectra of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers with different buffer layer

annealing durations. It can be seen that the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers show a typical two-mode behavior, which are around 234 cm^{-1} and 252 cm^{-1} , corresponding to LO-phonon modes of InAs and GaAs [13], respectively, for all samples. It is known that Raman scattering is determined by the overlap integral of electrons, phonons and photons. The residual strain in the epilayer will introduce defects and then broaden the Raman peaks and asymmetry of the Raman scattering line shape [14]. Therefore, the full-width at half-maximum (FWHM) and the asymmetry ratio of Raman scattering spectra can characterize the crystalline quality of samples. For $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ materials, the GaAs-like LO-phonon modes still dominate the Raman spectrum [15]. So, the FWHM and the asymmetry ratio (Γ_a/Γ_b) of GaAs-like LO-phonon peak can be employed to characterize the quality of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ materials. Γ_a and Γ_b are two half-widths at half-maximum of GaAs-like LO-phonon peak which are displayed in the inset of Fig. 2. The FWHM and the asymmetry ratio (Γ_a/Γ_b) of GaAs like LO phonon peak as a function of thermal annealing duration are shown in Fig. 3. The value of FWHM and the asymmetry ratio of samples A_1 , A_2 , A_3 , A_4 , A_5 are 9.18, 9.04, 8.63, 8.84, 8.95 cm^{-1} and 1.39, 1.38, 1.30, 1.35, 1.36, respectively. It is obvious that sample A_3 has the minimum FWHM and Γ_a/Γ_b , confirming that the crystal quality of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers is improved by thermal annealing process of buffer layers, which is consistent with the DCXRD and Hall measurements.

It is clear that the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ thermal annealing treatment of buffer layer can effectively improve the crystalline quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. In our experiments the growth conditions are fixed but the buffer's thermal annealing duration is varied. In order to gain further insights into the effect of thermal annealing on the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layer, five buffer layers named a1, a2, a3, a4, and a5, were prepared and examined by AFM. The buffer layers are grown under the same conditions as those in samples A_1 , A_2 , A_3 , A_4 , and A_5 , respectively. The surface morphology of the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layer is taken over an ($3 \times 3\ \mu\text{m}^2$) area and shown in Fig. 4(a1)–(a5), respectively. It is clear that the surface of buffer layers have a granular surface. But the surface roughness increases, and the grain size becomes larger after annealing for different durations. It is known that the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer A_3 grown on the buffer layer a3 has the best quality, implying that the quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers is closely related to the surface morphology of buffer layers. A similar phenomenon of the change of surface morphology was observed in low-temperature AlN buffer used in GaN growth in [16]. Therefore, the model can be used to explain the changes of our results. When the buffer was thermal treated for less than 5 min, the buffer layer has small grain size and high nuclei density. The $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ islands in the initial growth stage will coalesce quickly and a lot of formed dislocations will go through the $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers, leading to a poor quality. When the buffer was thermal annealing for longer than 5 min, the buffer layer has too large grain size and too low nuclei density, it

will take too long time for the growth of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ islands, and the quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers will also become bad. That is, a suitable grain size and nuclei density could improve the quality of the subsequent $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer. Therefore, optimization of buffer layer thermal annealing duration is an effective way to improve the quality of $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer by two-step growth method.

4. Conclusions

In this study, $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer has been grown using $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ buffer layer on InP substrate with the two-step growth technique. The influence of buffer layer thermal annealing duration on $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer grown on InP substrate was discussed. It was found that the thermal annealing of the buffer layers improved the structural properties of subsequent $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayers. The $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}$ epilayer exhibits best crystalline quality when the buffer layer thermal annealing for 5 min at $530\text{ }^\circ\text{C}$. This observation can be explained by the change of surface morphology of the buffer layer after thermal annealing treatment.

Acknowledgment

This work was supported by the National Natural Science Foundation of the China under Grant Nos. 50632060 and 50372067.

References

- [1] M.A. di Forte-Possion, C. Brylinski, J. Cryst. Growth 124 (1992) 782–791.
- [2] S.L. Murray, F.D. Newman, C.S. Murray, D.M. Wilt, M.W. Wanlass, P. Ahrenkiel, R. Messham, R.R. Siegiej, Semicond. Sci. Technol. 18 (2003) s202–s208.
- [3] Y.G. Zhang, Y. Gu, C. Zhu, G.Q. Hao, A.Z. Li, T.D. Liu, Infra. Phys. Technol. 47 (2006) 257–262.
- [4] R.U. Martinelli, T.J. Zamerowski, P.A. Longerway, Appl. Phys. Lett. 53 (1988) 989–991.
- [5] M. Wada, H. Hosomatsu, Appl. Phys. Lett. 64 (1993) 1265–1267.
- [6] Z.C. Zhang, S.Y. Yang, F.Q. Zhang, B. Xu, Y.P. Zeng, Y.H. Chen, Z.G. Wang, J. Cryst. Growth 247 (2003) 126–130.
- [7] D.S. Kim, S.R. Forrest, M.J. Lange, M.J. Cohen, G.H. Olsen, R.J. Menna, R.J. Paff, J. Appl. Phys. 80 (1996) 6229–6234.
- [8] T.M. Zhang, G.Q. Miao, Y.X. Jin, J.C. Xie, H. Jiang, Z.M. Li, H. Song, Microelectron. J. 38 (2007) 398–400.
- [9] T.M. Zhang, G.Q. Miao, Y.X. Jin, S.Z. Yu, H. Jiang, Z.M. Li, H. Song, J. Alloy. Compd. 458 (2008) 363–365.
- [10] T.M. Zhang, G.Q. Miao, Y.X. Jin, S.Z. Yu, H. Jiang, Z.M. Li, H. Song, J. Alloy. Compd. 472 (2009) 587–590.
- [11] S.Z. Chang, T.C. Chang, J.L. Shen, S.C. Lee, Y.F. Chen, J. Appl. Phys. 74 (1993) 6912–6918.
- [12] F. Xiu, Z. Yang, D. Zhao, J. Liu, K.A. Alim, A.A. Balandin, J. Cryst. Growth 286 (2006) 61–65.
- [13] S. Emura, S. Gonda, Y. Matsui, H. Hayashi, Phys. Rev. B 38 (1988) 3280–3286.
- [14] Z.G. Qian, W.Z. Shen, H. Ogawa, Q.X. Guo, J. Phys.: Condens. Matter 16 (2004) R381–414.
- [15] J. Groenen, G. Landa, R. Carles, J. App1. Phys. 82 (1997) 803–809.
- [16] D.G. Zhao, J.J. Zhu, Z.S. Liu, S.M. Zhang, H. Yang, Appl. Phys. Lett. 85 (2004) 1499–1501.