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Anomalous luminescence behavior in the InAlGaN thin film

Sheng-Yao Hu [a,*], Yueh-Chien Lee [b], Zhe-Chuan Feng [c], Shi-Hong Yang [d]

[a] Department of Electrical Engineering, Tung Fang Design University, Hunei Township, Kaohsiung County, 82941, Taiwan
[b] Department of Electronic Engineering, Tung Nan University, Shen-Keng Township, Taipei County, 22202, Taiwan
[c] Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei 10617, Taiwan
[d] Department of Electrical Engineering, National Taiwan Ocean University, Keelung 20224, Taiwan

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ABSTRACT

Photoluminescence (PL) spectra of a quaternary alloy $In_{0.014}Al_{0.105}Ga_{0.881}N$ thin film grown by low pressure metalorganic chemical vapor deposition (MOCVD) are studied experimentally in the temperature range of 10–300 K. It is shown that the temperature dependence can be well studied by the Eliseev's model to characterize the scale of the exciton-localization effects for the exciton localization energy. Moreover, the Urbach energy was determined from an analysis of the low-energy side of the PL lineshape. From the temperature dependence of Urbach energy, the value of Urbach energy can be described by the Einstein oscillator model which takes into consideration the contributions from both the thermal and structural disorders.

1. Introduction

Studies of the optical properties of quantum-confinement structures based on InAlGaN quaternary alloys are an important heterostructure engineering tool and have the ability of tuning the direct band gap in the wide energy range [1–3]. The band gap energies of the end-point compounds are 0.65 eV for InN, 3.43 eV for GaN and 6.04 eV for AlN at room temperature (RT) [1]. Such a capability has facilitated enormous potential in ultraviolet (UV) and deep UV optoelectronic device applications [1–3]. So far, the high efficiency of InGaN-based light emitting diodes (LEDs) and laser diodes (LDs) is generally attributed to a strong In-induced exciton localization that prevents carriers to reach nonradiative recombination centers (NRCs) [1]. Therefore, efficient visible LEDs and LDs produced by InGaN ternary alloys are commercially available despite a very high dislocation density due to heteroepitaxial growth [5]. Moreover, AlGaN UV-LEDs show a much lower efficiency than InGaN-based LEDs due to difficulties to achieve p-type conductivity with increasing Al content and to the lack of efficient exciton localization, which makes carriers very sensitive to NRCs [5]. Instead of the InGaN or AlGaN systems, quaternary InAlGaN alloys have been proposed to improve UV-LEDs [2]. Because quaternary InAlGaN alloys can provide a separate control of the band gap energy and the lattice parameter, thus allowing a reduction of strain-related defects [5,6] and the built-in electric field in quantum well heterostructures grown along the ***c***-axis [5,7]. Additionally, In incorporation into AlGaN may induce exciton localization leading to an increasing localization energy for higher In concentrations [1,5]. Up to now, the basic properties and parameters of InGaN or AlGaN ternary alloys, the determination of the band gap and its variation with temperature and composition have been discussed [5,8,9], however, few reports have focused on the anomalous luminescence behavior based on the structure of InAlGaN thin films [3–5].

In this work, we analyze the photoluminescence (PL) spectra of the heterostructures with a thin InAlGaN layer, determined parameters and mechanism of the charge-carrier localization. To obtain quantitative characteristics of the exciton localization in this investigated sample, we calculate the parameter σ which is a measure of the dispersion in the exciton-localization energy and the Urbach energy E_U. The parameter σ was determined in the context of Eliseev's model [9,10] which was shown to describe satisfactorily the experimental temperature dependences of the spectral position of the PL peak that specifies the radiative and nonradiative processes in the structure of InAlGaN sample.

2. Experimental

A quaternary alloy sample of $In_{0.014}Al_{0.105}Ga_{0.881}N$ thin film was grown by low pressure metalorganic chemical vapor deposition (MOCVD). $In_{0.014}Al_{0.105}Ga_{0.881}N$ thin film with a thickness of about 250 nm was grown on the 2 μm thick GaN/Al_2O_3 substrate by the low pressure MOCVD with around 25 nm AlN buffer layer to avoid cracking in the structure. X-ray photoelectron spectroscopy (XPS) was employed to measure the chemical composition of In, Al and Ga in this as-grown film. The temperature dependence PL measurements were carried out inside a closed-cycle He cryostat varied from 10 to 300 K by a modified and computer controlled LakeShore 321 model temperature controller with an accuracy of ±0.5 K using a 5 mW/cm^2 microchip laser operating at 266 nm as an excitation source. The PL signals were

* Corresponding author. Tel.: +886 7 6939632x102; fax: +886 7 6932348.
E-mail address: shenghu2729@yahoo.com (S.-Y. Hu).

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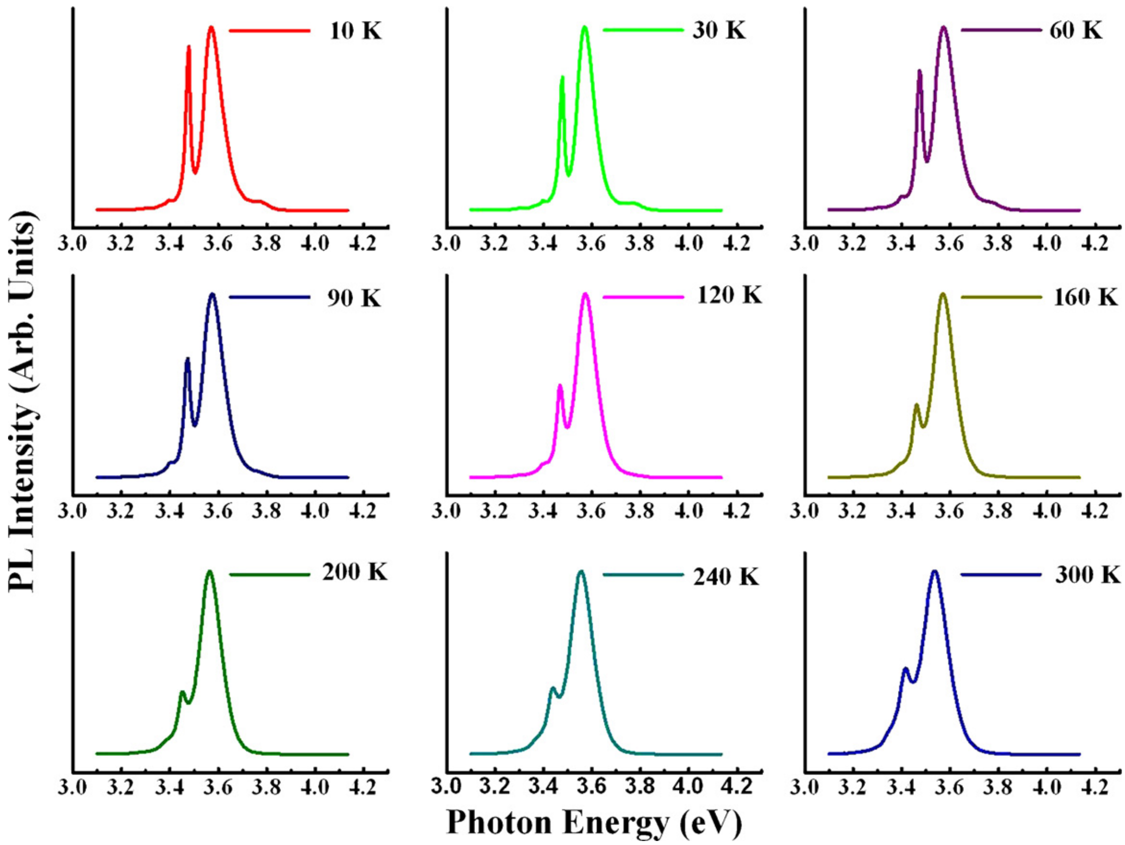

Fig. 1. PL spectra from the $In_{0.014}Al_{0.105}Ga_{0.881}N$ and the GaN substrate revealing the significant emissions at several different temperatures in the range of 10–300 K. Two main features are observed at around 3.60 and 3.46 eV, at low temperature of 10 K, corresponding to the onset of the $In_{0.014}Al_{0.105}Ga_{0.881}N$ exciton band and to the GaN substrate absorption, respectively.

recorded using a spectrometer (Acton SP-2150i) with a 1200 grooves/mm grating and detected using a cooled GaAs photomultiplier tube.

3. Results and discussion

Fig. 1 shows the PL spectra from the $In_{0.014}Al_{0.105}Ga_{0.881}N$ and the GaN substrate revealing the significant emissions at several different temperatures in the range of 10–300 K. Two main features are observed at around 3.60 and 3.46 eV, at low temperature of 10 K, corresponding to the onset of the $In_{0.014}Al_{0.105}Ga_{0.881}N$ exciton band and to the GaN substrate absorption, respectively. With increasing temperature, the emission intensity of the peak at the low-energy side decreases more quickly than that of the high-energy side, and it nearly becomes a shoulder at the temperature of 300 K. In this work, we would like to concentrate on the study of the higher energy side which is due to the $In_{0.014}Al_{0.105}Ga_{0.881}N$ energy level.

The shifts in the PL peak energy (E_{PL}) of $In_{0.014}Al_{0.105}Ga_{0.881}N$ thin film with temperature are displayed in Fig. 2. The anomalous luminescence peak energy varies with temperature, with an often-called S-shaped behavior is observed where the E_{PL} first redshift, then blueshift and shows monotonous redshift above 100 K. The temperature-dependent E_{PL} of InAlGaN is quite different comparing with the temperature dependence of the GaN band gap (shown as the inset). This emission shift is typical of disordered systems and is attributed to alloy potential fluctuations in the layers [4,10–12]. A similar phenomenon has been reported in the PL spectra of the structure with $In_xAl_yGa_{1-x-y}N$ layers in a broad temperature range of 15–300 K by Chen et al. [4] to suggest that the localized states leading to the unusual behavior may come from the size fluctuations due to the inhomogeneous distribution of InGaN-like clusters and the larger InGaN-like cluster has the lower energy state corresponding to the stronger localized effect [4].

In Fig. 2, three temperature regions can be defined, labeled A, B and C, and corresponding to a redshift, blueshift and redshift behavior of the E_{PL}. T_1 and T_2 are the terminal temperatures of regions A and B, respectively. In region A of the temperature range from 10 to 30 K, at $T < T_1$ (where T_1 is the temperature of maximum exciton localization), it is assumed that the exciton can recombine, being trapped in the local minima of the potential. As the

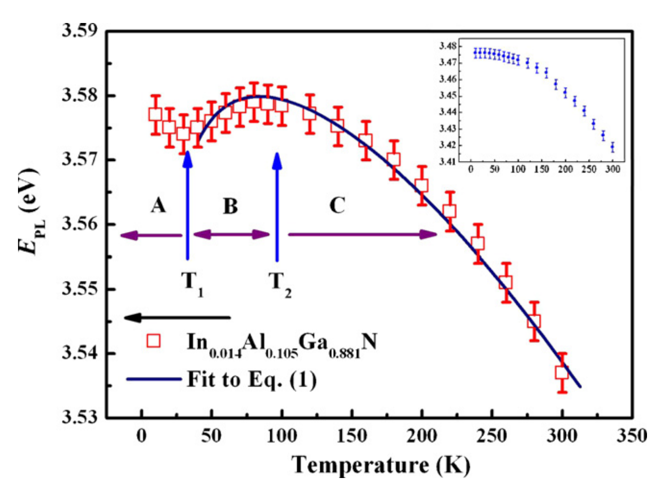

Fig. 2. The PL peak energy as a function of temperature for $In_{0.014}Al_{0.105}Ga_{0.881}N$ thin film (open squares) and the inset is the temperature dependence of the GaN band gap (closed circles). The solid curve is least squares fit to Eq. (1) according to Eliseev's model.

temperature rises, weakly localized charge carriers become thermally activated and can either recombine nonradiatively or make a transition to the deeper localized states, which results in a shift of the PL peak to lower energies [4,12]. At higher temperatures of region B from 30 to 100 K, the thermal redistribution of the charge carriers leads to an increased occupation of higher-energy states, thus the PL peak begins to shift to higher energies, and a maximum is attained at $T = T_2$, the temperature corresponding to the onset of the exciton delocalization [4,12]. When the temperature is raised still further, the PL peak will shift monotonously to lower energies (a redshift). Consequently, in region C (above 100 K) the E_{PL} follows the temperature dependence of the excitonic band gap. In order to describe the temperature dependence of the PL peak position in $In_{0.014}Al_{0.105}Ga_{0.881}N$ sample under study, we used the well-known model suggested by Eliseev [10,13]. Fig. 2 shows the experimentally determined temperature dependence for the energy of the PL peak in $In_{0.014}Al_{0.105}Ga_{0.881}N$ which can be described well in the context of Eliseev's model. In Eliseev's model, the temperature dependence of the PL peak position is expressed as:

$$E_g(T) = E_g(0) - \frac{\alpha \times T^2}{T + \beta} - \frac{\sigma^2}{k_B T} \quad (1)$$

where $E_g(0)$, α and β are the Varshni fitting parameters, k_B is the Boltzmann constant, σ is the localization parameter which gives an estimate of the energy of localization, and T is the measured temperature.

At low temperatures, the PL originates from the recombination of localized excitons. At temperatures exceeding the exciton-delocalization temperature T_2 (about 100 K), the behavior of the PL peak is determined not only by localized excitons occupying states in the tails of the density of states but also by a considerable contribution from delocalized excitons. Moreover, at higher temperatures (above 100 K), the PL emission peak shows monotonous redshift as a result of temperature induced shrinkage of the band gap of $In_{0.014}Al_{0.105}Ga_{0.881}N$.

From the context of Eliseev's model, the fitting yields value of the parameter σ characterizing the dispersion of the exciton-localization energy at around 10 ± 2 meV and the temperature coefficient, α is around 3.3×10^{-4} eV/K and $\beta \sim 730 \pm 30$ K is related to the Debye temperature (Θ_D). Above 100 K, the exciton localization energy becomes overshadow by the temperature-induced band shrinkage and lead to a redshift of the PL peak.

We further discuss the mechanisms of the tail states in our sample, since the linewidth variation has to be related with the behavior of the tail states. The low-energy side of the PL lineshape being mainly related to the localized exciton states whose energy distribution is described by the Urbach tail of the density of states [12,14]. Therefore, the Urbach energy (E_U) can be estimated by analyzing the shape of the spectral lines [12,14]. To determine the E_U, we focus on the PL spectrum in the low-energy side and the Urbach tail is described by an exponential function $\rho(E) \propto \exp(E/E_U)$ [12,14]. Utilizing this analysis, it is possible to determine the typical mean localization energy of excitons in the structure containing thin $In_{0.014}Al_{0.105}Ga_{0.881}N$ layer.

On the higher energy side of the main emission peak corresponding to the onset of the $In_{0.01}Al_{0.11}Ga_{0.88}N$ exciton band can be clearly observed from our PL spectra within 10–300 K. The shape of the low-energy tail of the experimental PL spectrum was analyzed by fitting with a Gaussian curve. The measured PL spectrum at 60 K was displayed in the upper left corner inset of Fig. 3, together with the fitted Gaussian curve as the open circles. The low-energy side of the fitted Gaussian curve can then be fitted by the exponential function and E_U is then evaluated to be about 34 meV. Therefore, a similar fitting procedure can be performed to the other experimental results to obtain the variation of E_U against temperature for $In_{0.014}Al_{0.105}Ga_{0.881}N$ and is shown in Fig. 3 as the closed triangles.

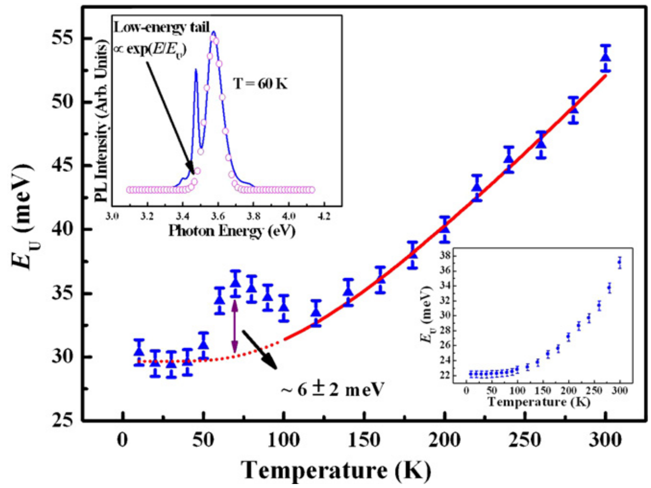

Fig. 3. Variation of Urbach energy (E_U) against temperature for $In_{0.014}Al_{0.105}Ga_{0.881}N$ as the closed triangles. The solid curve represents a fit to Eq. (2). The upper left corner inset is measured PL spectrum at 60 K displayed together with one Gaussian curve fitted as the open circles and the E_U is evaluated to be about 34 meV. The extended dotted line is a theoretical fitted curve to estimate the deviated value to be around 6 ± 2 meV. For comparison purpose, the E_U of GaN is shown in the lower right corner inset as the closed circles.

According to the theory of Urbach rule, the E_U should increase with temperature increasing in the absence of tail states due to thermal broadening. This is observed for our sample of $In_{0.014}Al_{0.105}Ga_{0.881}N$ except at the temperature range where the exciton localization effect is dominant. Those observed anomalous E_U with increasing temperature might be a characteristic of localization effect [12]. For comparison purpose, the E_U of GaN is shown in the lower right corner inset of Fig. 3 as the closed circles.

Further consideration of the E_U in $In_{0.014}Al_{0.105}Ga_{0.881}N$, can be performed as follow: The contribution to E_U as a function of temperature for $In_{0.014}Al_{0.105}Ga_{0.881}N$ can come from both static structural and dynamic phonon disorders [15,16]. E_U is directly corresponded to the thermal-induced disorder in semiconductor of high crystalline quality, but it becomes larger because of the contributions from both thermal and structural disorders for non-ideal single crystals. Hence, from the study of the temperature dependence of E_U, it is possible to get some information about the interaction of electrons/excitons with phonons. The value of E_U can be described by the Einstein oscillator model [15,16], which takes into consideration the contributions from both the thermal and structural disorders. The contributions to E_U are assumed to be a linear addition of the thermal and structural disorders. The model can be expressed as the following:

$$E_U = A\left(\frac{1}{\exp(\Theta_E/T) - B}\right) + B \quad (2)$$

where the first term is related to the thermal-induced disorder with temperature dependence (A is a constant), B is related to the temperature-independent structural disorders and Θ_E is the Einstein temperature related to the Debye temperature by $\Theta_E = 3/4\Theta_D$.

The best fit with the empirical relation of Eq. (2) shown by a solid line in Fig. 3, is obtained with $\Theta_E = 550 \pm 25$ K. The estimated value of constant A is about 107 meV and that of B is about 32 meV. Since the structural disorder is temperature independence, the structural disorder contributes 32 meV to the E_U from 10 to 300 K. The thermal-induced disorder is about 0 meV at 10 K and would be increased with increasing temperature to be about 20 meV at 300 K. Therefore, we suggest that the structural disorder might dominant at low temperature and the E_U can be increased with increasing temperatures by the thermal-induced disorder.

Since the structural disorders in (In, Al, Ga)-nitride quaternary alloys are expected to be related to the alloy compositional fluctuations [17]. The existence of localized excitons has often been suggested in the InGaN films and quantum well (QW) structures because of the In fluctuation [18] and the quaternary $In_xAl_yGa_{1-x-y}N$ layers have been considered to be an InGaN-like alloys by Chen et al. [4]. Then, it seems to be reasonable that the anomalous E_U in the $In_{0.014}Al_{0.105}Ga_{0.881}N$ comes from the localized states and these states can be attributed to local compositional fluctuation in the $In_xAl_yGa_{1-x-y}N$ film and the $In_xAl_yGa_{1-x-y}N$ material system because mixing of In, Al and Ga atoms occurs on one of the sublattices [17]. Furthermore, there exists strong immiscibility between the InN-like or InGaN-like or even high-In and low-In InAlGaN nanoscale clusters can be easily formed so these clusters become the localized center of excitons (carriers) [17].

Based on the above results, localization caused by structural disorder may yield localized positions with different energies, therefore localized carriers can transfer from higher energy positions to lower energy positions through a relaxation process. Most of the photogenerated carriers relax to the energy minimum of the excited state and then drop back to the ground state by radiative or nonradiative recombination processes but some carriers may be trapped in a localized state, originating from the structural disorder in the surface [19]. As a rule, the E_U can be increased with temperatures due to thermal broadening and this is observed for the E_U of GaN in Fig. 3. So, it implies that no localization effect exists in the GaN. However, the E_U of our $In_{0.014}Al_{0.105}Ga_{0.881}N$ decreases with the temperature from 10 to 30 K, increases from 30 to 70 K as the population of tail states increases, then decreases from 70 to 100 K as the de-trapping occurs. As the temperature increases further from 100 to 300 K, thermally excited carriers in the delocalized states are captured to the nonradiative recombination centers. Additionally, the nonradiative transition dominates the recombination process from 100 to 300 K, and the E_U increases as the temperature increases. To quantify the anomalous E_U behavior, we also measure the mismatch between experimental data and theoretical fitted curve (extended dotted line). We measure the deviated value at around the temperature of E_U blueshift maximum. The measured deviated value is around 6 ± 2 meV and is also found to correlate closely with the σ (10 ± 2 meV) value using the PL spectra. However, the value using the second method is lower than the one using the Eliseev's model. The above discrepancy might be from the indirect way in which the anomalous E_U behavior relates to the localization effect.

4. Conclusion

Eliseev's model and Urbach rule have been used to characterize the quaternary alloy in the structure containing thin $In_{0.014}Al_{0.105}Ga_{0.881}N$ film separated by GaN layer. Temperature dependence of the PL peak energy in the range of 10–300 K exhibits anomalous luminescence (S-shaped) behavior in the lower temperature region. The dependence of PL peak position on temperature indicates, at about 100 K, the bound excitons are de-trapped to become free excitons and free exciton emissions becomes dominant above 100 K. The Urbach energy for the structure under study is determined by analyzing the low-energy side of the PL lineshape. The measured exciton-localization energy σ is also found to correlate closely with the deviated value found using the low-energy PL lineshape for the Urbach energy. According to the Einstein oscillator model, the thermal-induced disorder is weaker at low temperature and the structural disorder is dominant at room temperature.

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References

[1] S.F. Chichibu, A. Uedono, T. Onuma, B.A. Haskell, A. Chakraborty, T. Koyama, P.T. Fini, S. Keller, S.P. Denbaars, J.S. Speck, U.K. Mishra, S. Nakamura, S. Yamaguchi, S. Kamiyama, H. Amano, I. Akasaki, J. Han, T. Sota, Nat. Mater. 5 (2006) 810.
[2] H. Hirayama, J. Appl. Phys. 97 (2005) 091101.
[3] E. Monroy, N. Gogneau, F. Enjalbert, F. Fossard, D. Jalabert, E. Bellet-Amalric, L.S. Dang, B. Daudin, J. Appl. Phys. 94 (2003) 3121.
[4] C.H. Chen, L.Y. Huang, Y.F. Chen, H.X. Jiang, J.Y. Lin, Appl. Phys. Lett. 80 (2002) 1397.
[5] S. Fernández-Garrido, J. Pereiro, F. González-Posada, E. Muñoz, E. Calleja, A. Redondo-Cubero, R. Gago, J. Appl. Phys. 103 (2008) 046104.
[6] M.A. Khan, J.W. Yang, G. Simin, R. Gaska, M.S. Shur, H.-C. zur Loye, G. Tamulaitis, A. Žukauskas, D.J. Smith, D. Chandrasekhar, R. Bicknell-Tassius, Appl. Phys. Lett. 76 (2000) 1161.
[7] M. Zamfirescu, A. Vinattieri, M. Gurioli, M. Androulidaki, N.T. Pelekanos, A. Georgakilas, Phys. Status Solidi (c) 2 (2005) 3941.
[8] S.O. Usov, A.F. Tsatsulnikov, V.V. Lundin, A.V. Sakharov, E.E. Zavarin, D.S. Sizov, Y.G. Musikhin, N.A. Bert, E.M. Arakcheeva, N.N. Ledentsov, Semicond. Sci. Technol. 22 (2007) 528.
[9] K.B. Lee, P.J. Parbrook, T. Wang, F. Ranalli, T. Martin, R.S. Balmer, D.J. Wallis, J. Appl. Phys. 101 (2007) 053513.
[10] P.G. Eliseev, J. Appl. Phys. 93 (2003) 5404.
[11] M. DeVittorio, G. Coli, R. Rinaldi, G. Gigli, R. Cingolani, D. De Salvador, M. Berti, A. Drigo, F. Fucilli, T. Ligonzo, V. Augelli, A. Rizzi, R. Lantier, D. Freundt, H. Luth, B. Neubauer, D. Gerthsen, Solid-State Electron. 44 (2000) 465.
[12] R.J. Potter, N. Balkan, J. Phys.: Condens. Matter 16 (2004) S3387.
[13] V.P. Varshni, Physica 34 (1967) 149.
[14] H.P.D. Schenk, M. Leroux, P. de Mierry, J. Appl. Phys. 88 (2000) 1525.
[15] Z. Yang, K.P. Homewood, M.S. Finney, M.A. Harry, K.J. Reeson, J. Appl. Phys. 78 (1995) 1958.
[16] G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, Y. Goldstein, Phys. Rev. Lett. 47 (1981) 1480.
[17] D.-B. Li, X. Dong, J. Huang, X. Liu, Z. Xu, Z. Zhang, Z. Wang, Appl. Phys. A 80 (2005) 649.
[18] S. Nakamura, S. Pearton, G. Fasol, The Blue Laser Diode: The Complete Story, 2nd ed., Springer, NY, 2000.
[19] Y.C. Lee, Y.L. Liu, W.Z. Lee, C.K. Wang, J.L. Shen, P.W. Cheng, C.F. Cheng, T.Y. Lin, Phys. Status Solidi (a) 201 (2004) 3188.