IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Defect-related luminescence of Mg-doped n-GaN grown by hydride vapour-phase epitaxy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 11103

(http://iopscience.iop.org/0953-8984/10/48/029)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.210
The article was downloaded on 14/05/2010 at 18:04

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **10** (1998) 11103–11110. Printed in the UK PII: S0953-8984(98)96441-4

Defect-related luminescence of Mg-doped n-GaN grown by hydride vapour-phase epitaxy

Chul Lee†, Jae-Eun Kim†, Hae Yong Park†, S T Kim‡ and H Lim§

† Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

‡ Department of Materials Engineering, Taejon National University of Technology, Taejon 300-172, Korea

§ Department of Electronic Engineering, Ajou University, Suwon 442-749, Korea

Received 3 August 1998

Abstract. We study photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Mg-doped n-GaN grown by hydride vapour-phase epitaxy. Defect-related red and blue emission bands around 1.85 eV and 2.90 eV, respectively, are observed in addition to the yellow emission band. The red and the blue emission bands are attributed to the recombinations involving the same Mg-related defects according to the result of the thermal annealing experiment. The PLE spectra of the red, the yellow, and the blue emission bands show that all of these emission bands can be interpreted in terms of a configuration coordinate (CC) diagram. The blue emission at 2.90 eV is attributed to the transition from the conduction band to the Mg-related deep acceptors. The CC diagram shows that the yellow luminescence is due to the transition from a deep donor state to a shallow acceptor state. A possible origin of the deep donor level is also discussed.

1. Introduction

The group III nitrides (GaN, AlN, InN) have a wide direct bandgap (e.g., 3.503 eV for GaN at low temperature [1]) and have been recognized as important materials for application in short-wavelength light-emitting devices. The first blue cw laser of III nitrides operating at room temperature has been demonstrated recently [2]. In spite of the progress in the field of optoelectronic devices, substantial areas of physical properties still need further investigation. One of these is the origin of the yellow luminescence in GaN. Several models have been proposed to explain the origin of the yellow band. The model proposed by Glaser *et al* attributes the yellow luminescence to the transition from a deep donor state to an effective mass-like acceptor state [3]. Another model proposed by Ogino and Aoki [4] and Hofmann *et al* [5], asserts that the yellow luminescences are caused by the process of recombination of the shallow donors and the deep acceptors. Other models proposed to explain the properties of deep defects in GaN are still under debate. Anyway, as the existence of defect-related emission band reduces the efficiency of the blue emission from GaN, it is important to elucidate the mechanism of defect-related emission and to find a way to suppress it.

In this work we present photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Mg-doped n-GaN as a function of temperature. In the PL measurements, defect-related red, yellow, and blue emission bands are observed. The temperature dependences of the excitation spectra for the red, the yellow, and the blue emission bands are

0953-8984/98/4811103+08$19.50 © 1998 IOP Publishing Ltd

studied to investigate the emission mechanism in terms of a configuration coordinate (CC) model. The mechanisms of these defect-related emissions will be discussed.

2. Experiment

The GaN films employed in this study were grown on (0001) planes of a sapphire substrate by hydride vapour-phase epitaxy (HVPE) method. Samples were unintentionally doped with residual Mg in the HVPE reactor. The typical film thickness was about 10 μm and the electron concentration at room temperature was around 10^{18} cm^{-3}. The samples were mounted in a cryostat and the sample temperature was measured using a Si diode temperature sensor. The PL spectra were obtained using a 325 nm He–Cd laser. For the PLE experiments, a 280 W tungsten–halogen lamp combined with a Spex 27 cm monochromator was used as an excitation light source. The luminescence was analysed by a Spex 75 cm monochromator provided with a 1200 grooves mm^{-1} grating. The dispersed emission was detected with a Hamamatsu R943-02 photomultiplier.

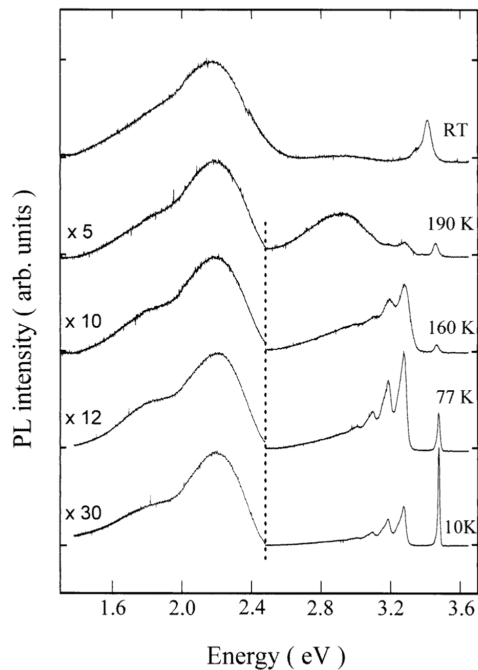

Figure 1. The photoluminescence of Mg-doped n-GaN as a function of temperature. Note that the blue emission band at about 2.90 eV appears above 160 K.

3. Results and discussion

Figure 1 shows the temperature dependence of the PL spectra observed in Mg-doped n-GaN. The PL peak at 3.47 eV is commonly observed for undoped GaN and is due to the decay of an exciton bound to a neutral donor (I_2) [6]. The peaks in the range 3.0–3.3 eV are known to be due to the donor-to-acceptor pair (DAP) recombination and its phonon replicas [7]. The energy position of the Mg shallow acceptor level, determined from the

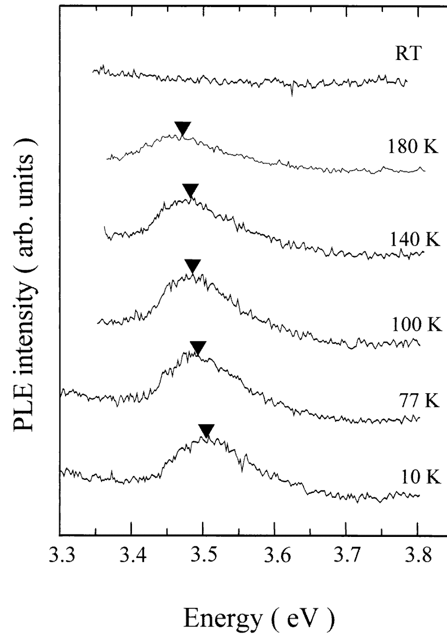

Figure 2. The temperature dependence of the PLE spectrum for the blue emission band at 2.90 eV. The inverted triangles indicate the bandgap energy. Note that the excitation peak is located at the bandgap energy.

DAP recombination peak energy using the reported value of 0.04 eV for the shallow donor energy level [8], is located at about 0.20 eV above the valence band maximum, showing a fairly good consistency with the reported Mg-related acceptor level [9]. In addition to these well-known peaks, we can also observe a broad yellow emission band at around 2.2 eV and a red emission band in the 1.8–1.9 eV range in the PL spectra of our Mg-doped samples. This red and yellow emission spectrum is similar to that of a Mg-implanted sample [10]. As the temperature increases above 160 K, a new peak appears at around 2.90 eV, and the DAP and its phonon replicas become quenched. The behaviour of our PL spectra with temperature is similar to that observed for Mg-doped [11] or Be-doped [12] p-GaN.

Smith *et al* [11] have already suggested that the 2.90 eV blue emission band is due to the transition from the conduction band to the doping-related deep-level centres (or complexes) on the basis of the temperature dependence of their PL spectra and the PL decay time. Figure 2 shows the PLE spectra of the blue emission band as a function of temperature. It is clear from the temperature dependence that the excitation peak is pinned at the bandgap energy. We also note in figure 1 that the blue emission band clearly appears above 160 K, when the DAP and its phonon replicas become quenched. These results mean that the 2.90 eV peak is related to the conduction band. Our PLE results indicate that the blue emission band is due to the recombination via the conduction band and Mg-related deep-level centres (or complexes), consistently with the interpretation made by Smith *et al* [11].

Thermal annealings in vacuum at 700 °C for 30 minutes have reduced the intensity of all of the defect-related emissions, but the ratio of the intensity of the red emission to that of the blue emission has not changed. This fact suggests that the red and the blue emission bands may have the same origin, i.e., the defect induced by the Mg doping. To

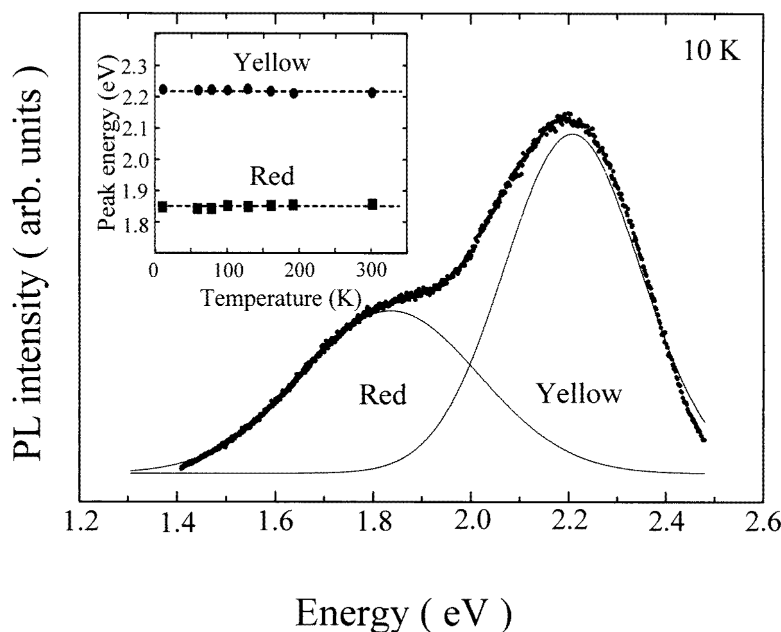

Figure 3. The deconvolution of the 10 K PL spectrum of Mg-doped n-GaN using the Gaussian line-shape functional form. Note that the peak energies are pinned at 1.85 eV and 2.22 eV for the red and the yellow emission bands, respectively, as temperature increases.

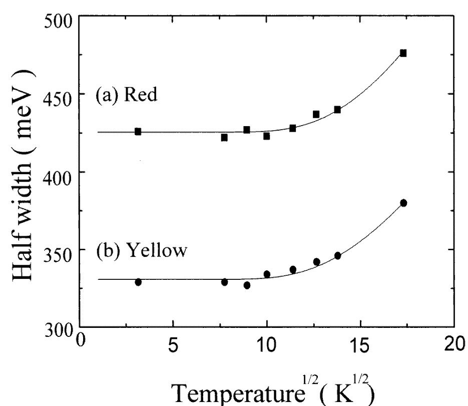

Figure 4. The variation of the halfwidth as a function of the square root of the temperature. The solid lines represent the fit of the form $W(T) = W(0)[\coth(\hbar w_e/2kT)]^{1/2}$. The best-fit results are $W(0) = 426$ and 331 meV, and $\hbar w_e = 56$ and 52 meV for the red and the yellow emission band, respectively.

discern the emission involving a complex from that involving isolated defects, we studied any possible variations of the peak energy and peak intensity of these emission bands with the temperature. For this purpose, as shown in figure 3, the overlapped PL spectrum in the range 1.4–2.4 eV (the red + yellow emission bands) was deconvoluted using the Gaussian line-shape functional form. The peak energies were determined to be 1.85 eV for the red and 2.22 eV for the yellow band. Both peak energies remain constant as temperature increases

(see the inset of figure 3). This means that deep levels must be related to both emissions. The halfwidths $W(T)$ for the red and the yellow emission bands are shown in figure 4 as a function of the square root of the temperature. If $W(T)$ can be described by a simple CC model, it follows the relation

$$W(T) = W(0)\left[\coth\left(\frac{\hbar w_e}{2kT}\right)\right]^{1/2} \tag{1}$$

where $W(0)$ is the halfwidth of the emission band at 0 K, and $\hbar w_e$ is the energy of the effective vibrational mode of the excited state [4]. When the above equation is fitted to the measured values, the best fitted values are $W(0) = 426$ and 331 meV, and $\hbar w_e = 56$ and 52 meV for the red and the yellow emission bands, respectively. The fact that the two emission bands have nearly the same vibrational energy of the excited state may imply that the same excited state (i.e., the same deep donor state) is involved in both emissions.

Figure 5 shows the PLE spectra of (a) the 1.85 eV (red) and (b) the 2.22 eV (yellow) luminescence peaks at various temperatures. We can notice that the red emission band, which is associated with the Mg-related deep acceptor level, has a strong excitation peak at 2.89 eV and a weak one at the bandgap energy. This means that the red emission band can be strongly excited by the 2.89 eV photons but only weakly by the photons of bandgap energy. From a close examination of the excitation spectra, we can see that the excitation efficiency of the red emission by the photons of bandgap energy increases as temperature is increased. This means, in turn, the existence of a potential barrier to the electron transfer from the conduction band (or shallow donors) to the deep donors which give rise to the red emission band. We thus attribute the red emission to the electron transition from the deep donors to the Mg-related deep acceptors. In this scheme, the direct excitation of 2.89 eV should be the transition from the Mg-induced defects to the deep donors (see the CC diagram in figure 6).

In figure 5(b) one can observe that the yellow emission band at 2.22 eV can be excited strongly by the 3.47 eV photons and weakly by the 2.89 eV photons. The overall features of our excitation spectrum are similar to those found in previous work, in which it was argued that the existence of the strong excitation peak related to the acceptor-bound exciton suggests a recombination starting from the shallow donors [5]. In our temperature-dependent PLE spectra, however, we can notice that the strong excitation peak at about 3.47 eV has a small shoulder on the high-energy side at low temperature and on the low-energy side at high temperature (see the arrows in figure 5(b)). The energy position of these shoulders follows exactly the temperature-dependent bandgap energy. Thus this excitation peak is actually composed of two components, the strong excitation pinned at 3.47 eV and the weak excitation of the bandgap energy. We observed that both the 2.89 eV and the bandgap energy excitations result in both the red and the yellow emissions, and the energies of the vibrational mode of the excited state are almost the same in the two emission bands. Thus we believe that the same deep donor, i.e., the same excited state, which has a potential barrier to the electron transfer from the conduction band (or shallow donor), must give rise to both emissions.

If the same deep donor is involved in both the red and the yellow emission bands, the yellow emission is then expected to involve the Mg shallow acceptor. Since the excited electrons are likely to come back to the impurity that they originated from, the excitation intensity of the 3.47 eV peak in the PLE spectra of the yellow emission should be much stronger than that of the 2.89 eV peak, as can be seen in figure 5(b). We can say the same thing for the excitation of the red emission. In our scheme, the red and the blue emission bands involve the same deep acceptor. But the electron transition starts from

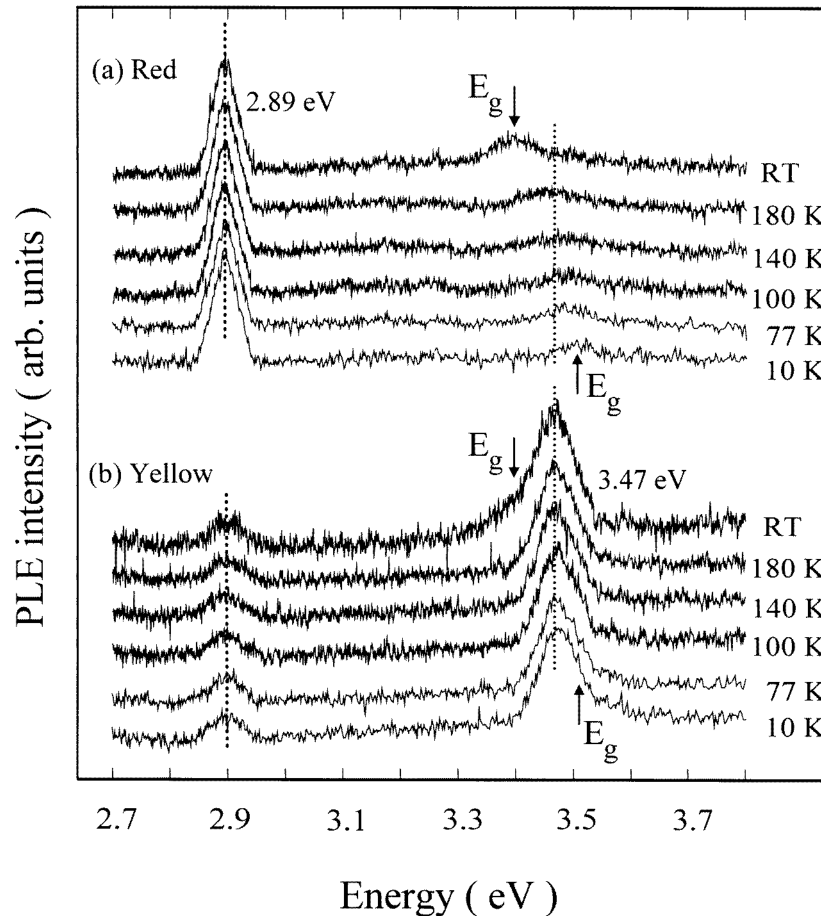

Figure 5. Photoluminescence excitation spectra of the (a) 1.85 eV and (b) 2.22 eV luminescence peaks as functions of temperature. Note that the excitation peak at around 3.47 eV in the PLE spectra of the yellow emission band is composed of two components, a strong excitation pinned at 3.47 eV and a weak excitation of the bandgap energy. The arrows indicate the bandgap energy excitations.

different configurations: the red emission from the deep donor state but the blue emission from the conduction band. The red and the yellow emission bands involve the same deep donor but different acceptors, i.e., the deep and the shallow acceptors, respectively. These recombination mechanisms can be explained consistently by the CC diagram in figure 6.

In the literature, two basically different recombination models have been proposed to explain the origin of the omnipresent 2.22 eV yellow PL band. In one model, the electron transition occurs from the deep intrinsic donors to the shallow acceptors [3]. In the other, the electron transition from a shallow donor state to a deep acceptor state was proposed [4, 5, 13, 14], even though different defects are assumed to be involved in the yellow luminescence. Our model for the yellow emission band is consistent with the arguments made by Glaser *et al* [3]. Even though the model involving the electron transition from the shallow donor state to the deep acceptor state is prevailing in the literature, this model cannot explain the intensity increase of the bandgap energy excitation with temperature.

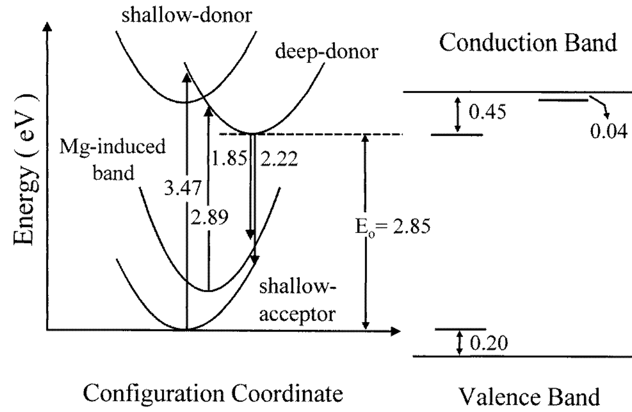

Figure 6. The configuration coordinate diagram employed to explain the mechanism of the yellow and red emission bands for Mg-doped GaN. This diagram is obtained using the experimentally measured PL and PLE results. Assuming the same curvature for the deep donor and the shallow acceptor, we found the activation energy of the deep donor to be about 0.45 eV. Also, the band model drawn on the right of the figure shows the depths of the defect states which are responsible for the observed emission bands.

This means that the shallow donors are not directly related to the yellow luminescence.

We believe that an intrinsic defect is the origin of the deep donor which gives the red and the yellow emission bands, as previous studies proposed that the intrinsic defect is responsible for the yellow band [3, 5, 14]. The first candidate for the intrinsic deep donor might be the nitrogen antisite at Ga sites (N_{Ga}), since the anion antisites usually give a deep donor level in III–V semiconductors. It is speculated that this N_{Ga}-related deep donor explains the reduction of the yellow emission band in Mg-doped GaN samples [13] and the increase in Se-doped GaN samples [14]. By occupying the Ga(N) sites, the Mg (Se) incorporated reduces (increases) the number of N_{Ga} antisites and also the yellow luminescences accordingly [13, 14]. However, it should be noted that the formation energy of N_{Ga} is larger than that of nitrogen vacancy (V_N) by about 6 eV when the Fermi energy is near the conduction band minimum [15]. Thus a complex defect containing V_N as one of its constituents would also be a good candidate for a deep donor giving a large lattice distortion.

Our CC diagram, based on the existence of these intrinsic deep donors, Mg shallow acceptors, and Mg-related deep acceptors, can explain all the defect-related sub-bandgap PL bands showing strong electron–lattice coupling. The existence of a thermal barrier between the shallow and the deep donor in our CC model can also explain the observed persistent photoconductivity in GaN [14]. After an electron is excited from the deep donor to the conduction band and/or the shallow donor state, the deep donor undergoes a large lattice relaxation which creates an energy barrier to prevent the photoexcited electron from returning to the original state. We also calculated the activation energy of the deep donor state in our CC model. We assume the same curvature for the configuration curves of the ground state and the excited state which are involved in the yellow emission. In the broad band formed by the overlapping of many phonon sidebands, the peak position of the zero-phonon band of energy E_0 is given by

$$E_0 = \frac{(E_{em} + E_{ab})}{2} \tag{2}$$

where E_{em} and E_{ab} are the emission and the excitation peak energies, respectively. Taking the experimentally observed values of 2.22 eV and 3.47 eV for E_{em} and E_{ab}, respectively, the activation energy of the deep donor is estimated to be about 0.45 eV. This value coincides with that observed for n-GaN by deep-level transient spectroscopy [16].

4. Conclusion

In conclusion, the measurements of the temperature-dependent PL of Mg-doped n-GaN grown by HVPE showed three emission bands: the red one centred at 1.85 eV, the yellow at 2.22 eV, and the blue at 2.90 eV. The results of thermal annealing experiments at 700 °C in vacuum suggest that the red and the blue emission bands are related to the same defect, probably the Mg-induced deep acceptor. The temperature dependence of the PLE spectra revealed some clues about the recombination mechanism relevant to these emission bands. Using a model CC diagram, we showed that all of the emission bands could be explained consistently. A possible origin of the deep donor, responsible for the red and the yellow emission bands, was also discussed.

Acknowledgments

This work was partially supported by the KOSEF through the SPRC in Jeonbuk National University and the BSRI program (97-2419) of the Korean Ministry of Education.

References

[1] Monemar B 1974 *Phys. Rev.* B **10** 676
[2] Nakamura S, Senoh M, Nagahame S, Iwasa N, Yamada T, Matushita T, Sugimoto Y and Kiyoku H 1997 *Appl. Phys. Lett.* **70** 1417
[3] Glaser E R, Kennedy T A, Doverspike K, Rowland L B, Gaskill D K, Freitas J A, Asif Khan M, Olson D T, Kuznia J N and Wickenden D K 1995 *Phys. Rev.* B **51** 13 326
[4] Ogino T and Aoki M 1980 *Japan. J. Appl. Phys.* **19** 2395
[5] Hofmann D M, Kovalev D, Steude G, Meyer B K, Hoffmann A, Eckey L, Heitz R, Detchprom T, Amano H and Akasaki I 1995 *Phys. Rev.* B **52** 16 702
[6] Dingle R, Sell D D, Stokowski S E and Ilegems M 1971 *Phys. Rev.* B **4** 1211
[7] Dingle R and Ilegems M 1971 *Solid State Commun.* **9** 175
[8] Fischer S, Wetzel C, Haller E E and Meyer B K 1995 *Appl. Phys. Lett.* **67** 1298
[9] Ilegems M and Dingle R 1973 *J. Appl. Phys.* **44** 4234
[10] Khasanov I Sh, Kuznetsov A V, Gippius A A and Semiletov S A 1983 *Sov. Phys.–Semicond.* **17** 187
[11] Smith M, Chen G D, Lin J Y, Jiang H X, Salvador A, Sverdlov B N, Botchkarev A, Morkoc H and Goldenberg B 1996 *Appl. Phys. Lett.* **68** 1883
[12] Salvador A, Kim W, Aktas O, Botchkarev A, Fan Z and Morkoc H 1996 *Appl. Phys. Lett.* **69** 2692
[13] Suski T, Perlin P, Teisseyre H, Leszcynski M, Grzegory I, Jun J, Bockowski M, Porowski S and Moustakas T D 1995 *Appl. Phys. Lett.* **67** 2188
[14] Chen H M, Chen Y F, Lee M C and Feng M S 1997 *Phys. Rev.* B **56** 6942
[15] Neugebauer J and Van der Walle C G 1994 *Phys. Rev.* B **50** 8067
[16] Gotz W, Johnson N M, Bour D P, Chen C, Liu H, Kuo C and Imler W 1996 *Mater. Res. Soc. Symp. Proc.* **395** 443