

## Optical properties of wurtzite GaN epilayers grown on A-plane sapphire

Andenet Alemu, Bernard Gil, and Michel Julier

Centre National de la Recherche Scientifique, Groupe d'Etude des Semiconducteurs, Université de Montpellier II, Case Courrier 074, 34095 Montpellier Cedex 5, France

Shuji Nakamura

R & D Department, Nichia Chemical Industries Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

(Received 27 June 1997)

The exciton binding energies are measured in GaN grown on A-plane sapphire. A value of  $25 \pm 1$  meV is found to be consistent with reflectance and photoreflectance experiments. This 25 meV value matches very well the results obtained on GaN epilayers grown on C-plane sapphire with strong biaxial compression, and seems to indicate that exciton energies in GaN epilayers are predominantly influenced by strain fields. From the in-plane anisotropy of optical response, we deduce a value of  $-2.4$  eV for the  $C_5$  deformation potential in GaN. [S0163-1829(98)03508-5]

Semiconductor physics at the end of the 1990s was strongly influenced by group-III nitrides. These materials offer the possibility to make light emitting diodes (LED's), which operate in the upper portion of the visible spectrum. Combined with red LED's based on semiconductors of the more classical III-V families, they can cover almost completely the chromaticity diagram. Besides this large scale market, commercial applications also exist which concern green, blue, and uv solid-state lasers.<sup>1</sup> The  $p$ -doping problem, the lack of native substrates, and the small critical thickness have long thwarted the realization of efficient electrical injection through nitride-based heterostructures. The most commonly used substrate is C-plane sapphire. When used, additional complication is brought to bear since the lattice of the GaN epilayer is rotated with respect to the underlying substrate.<sup>2</sup> As a consequence, it is impossible to align the easy cleavage planes of GaN with those of sapphire, which makes difficult the fabrication of laser cavities. This motivated Nakamura *et al.*,<sup>3</sup> who recently explored lasers grown on A-plane {11-20} sapphire substrates. Due to easy cleavage along the R plane {1-102}, they might be fairly promising for large scale production of nitride-based lasers. In this paper, we will first show that the material quality of the GaN epilayers deposited on these faces is good enough to allow us to make an accurate measurement of exciton binding energies. Second, we will determine the  $C_5$  deformation potential in GaN.

The determination of binding energies of the excitons for GaN grown on the C plane is currently attracting a lot of attention:<sup>4-15</sup> (i) On the one hand, the material GaN is interesting by itself for modern optoelectronic and electronic applications, as mentioned above: (ii) On the other hand, it can fascinate fundamental researchers since its valence-band physics is fairly complicated due to the combined effects of the hexagonal atomic coordination and residual built-in strain fields.<sup>16-18</sup> The determination of exciton binding energies in conventionally grown GaN has been intended through different indirect or direct approaches. Indirect measurements require, for instance, the temperature dependence of the free exciton photoluminescence intensity. We prefer more direct determination, which concerns measurements of different optical transitions by reflectance or photoreflec-

tance spectroscopy, their identification, and the calculation of the binding energy from straightforward application of quantum mechanics for hydrogenoid systems. In these approaches, the subtlety of the exercise lies in the identification of all optical transitions. Figure 1 displays a typical *unpolarized* photoluminescence spectrum (bottom of the figure), which shows free exciton luminescence in the lower and upper polariton branches<sup>19</sup> and a dominating extrinsic donor. Increasing the detection reveals free exciton luminescence in the energy region of structure B of the *unpolarized* reflectance spectrum (located in the middle of the figure). Identification of these transitions is unambiguously made by comparing the PL data with the reflectance ones or with the photoreflectance features reported in the top on the figure. This reflectivity spectrum is interesting in many aspects: from low to higher energies, transitions can be detected which a reflectance line-shape fitting at 3497, 3506.1, 3516,

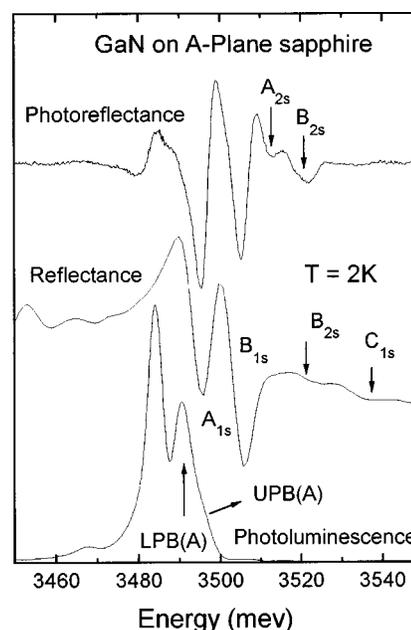


FIG. 1. Unpolarized photoluminescence (bottom), reflectance (middle), and photoreflectance spectra typical of GaN on A-plane sapphire.

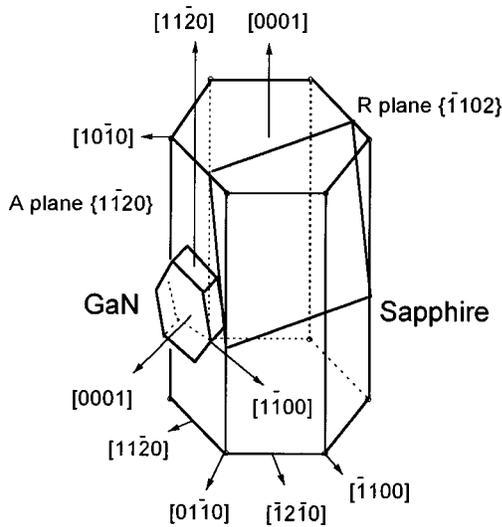


FIG. 2. Relative orientations of the crystallographic axes of GaN in case of heteroepitaxy on A-plane sapphire. Note that the  $\{0001\}$  plane of sapphire is parallel to the  $\{11-20\}$  plane of the GaN epilayer.

3525.5, and 3538.5 meV, respectively. Structures at 3497.1 and 3506.6 meV, 9.5 meV split, we attributed to  $1s$  A and  $1s$  B exciton states. We also find this 9.5 meV splitting between the lines at 3516 and 3525.5 meV. Therefore, the lines at 3516 and 3525.5 meV are attributed to  $2s$  states of the A and B excitons. From the 19 meV splitting between the fundamental states and the excited ones, we deduce a binding energy of  $25 \pm 1$  meV for the A and B free excitons. Photoreflectance experiments carried out by Tchounkeu *et al.*<sup>12</sup> and Shan *et al.*,<sup>11</sup> who have been studying exciton binding energy for GaN grown along the  $[0001]$  direction on sapphire<sup>11,12</sup> and SiC,<sup>11</sup> have led to very similar results. Shan *et al.*,<sup>11</sup> who have in particular performed a very careful line-shape fitting of the photoreflectance, which is not the case of Tchounkeu *et al.*,<sup>12</sup> reported the observation of weak lines labeled *a* and *b*, 8 meV split, which they have attributed to  $2s$  states of A and B excitons. They obtained binding energies of  $21 \pm 1$  meV.

At this stage, one could argue about a possible misinterpretation of our data. An answer can be given if we examine the orientation of the GaN epilayer with respect to the axes of the A-plane sapphire substrate. The  $\{0001\}$  plane of the GaN film grown on an A-plane sapphire substrate is parallel to the  $\{11-20\}$  face of the A-plane sapphire.<sup>1</sup> One side of the hexagonal GaN crystal is parallel to the *C* face of the A-plane sapphire substrate. As shown in Fig. 2, one clearly understands that the GaN cleaves along the  $\{1-100\}$  face when the sapphire substrate cleaves along its *R* plane. For the sake of completeness, we remind the reader that the angle between the  $\{1-100\}$  cleavage plane of GaN and the  $\{-1102\}$  *R* cleavage plane of sapphire is about  $2.4^\circ$ . When cooling down the sample, the thin GaN epilayer experiences strong in-plane anisotropic deformation between its  $[11-20]$  and  $[1-100]$  directions since the thermal expansion coefficient of sapphire is strongly anisotropic ( $\alpha_{\parallel c} = 8.5 \times 10^{-6} \text{ K}^{-1}$  and  $\alpha_{\perp c} = 7.5 \times 10^{-6} \text{ K}^{-1}$ ). As a consequence, the  $C_{6v}$  hexagonal symmetry of the GaN lattice is reduced to  $C_{2v}$  and we expect in-plane anisotropy of the optical response. This is shown in

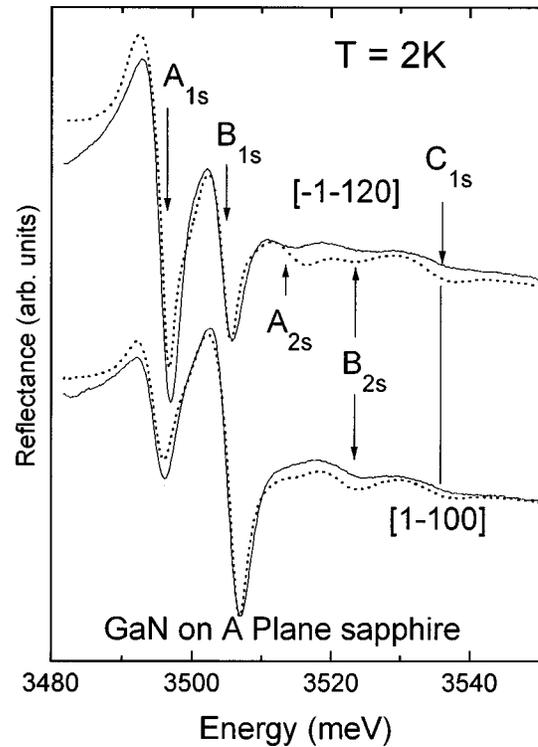


FIG. 3. Evolution of the intensity of the reflectance structures with in-plane orientation of the electric field: (a)  $[10-10]$  orientation, (b)  $[-12-10]$  orientation. Note the increase of  $A_{1s}$  is accompanied by a decrease of  $B_{1s}$  and makes it easier to detect  $A_{2s}$ . Arrows indicate the average positions of transverse excitonic polaritons. The experimental data and the line-shape fitting are plotted using full and dotted lines, respectively.

Fig. 3, where we report light polarization effects. Rotation of the incident electric field in the  $\{0001\}$  plane of GaN, between the  $[11-20]$  and  $[1-100]$  direction, modifies the relative intensities of A and B lines. The intensities of the transitions at 3516 and 3525.5 meV are independently following the intensities of the main structures as strong evidence of the proper identification of all radiative transitions in our sample. The fifth structure near 3538.5 meV is attributed to the *C* line, which is degenerated with the continuum of A and B. Consequently, it is very weak, excessively broad, but can be resolved, notwithstanding such a broadening. Circles in Fig. 4 illustrate the experimental variations of the intensities of the A and B lines obtained from a line-shape fitting of the reflectance for several spectra taken by rotating the polarization between the  $[10-10]$  direction ( $\theta = 0^\circ$ ) and the  $[-12-10]$  direction ( $\theta = 90^\circ$ ), in the  $\{0001\}$  GaN plane. Dashed lines in Fig. 3 illustrate the agreement with experiment (full lines). The *C* line was too broad and too weak to allow us to propose any dependence on the angle of polarization. The A, B, and C lines have been plotted in Fig. 5 in our dimensionless diagram,<sup>20</sup> which accounts for the variation of the splitting between these levels as a function of the strain for GaN epilayers grown on C-plane sapphire (to avoid the difficulty with the deformation potentials issue, the plot is made as a function of the position of the A line). This figure is an enriched version of the figure that one of us (B.G.) published in Ref. 21, and shows that a real reversal of the nature of the GaN top valence band from  $\Gamma_9$  to  $\Gamma_7$  is now experimentally

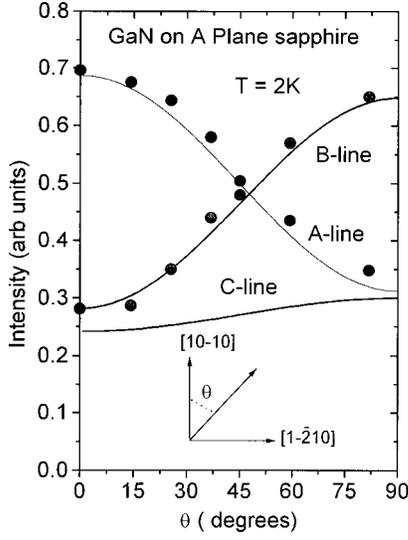


FIG. 4. Evolution of the oscillator strength of  $A$  and  $B$  lines as a function of the polarization of the photon (circles). Full lines represent the result of our calculation. Theoretical values for  $C$  line are magnified by a factor 8.

observed,<sup>22</sup> in agreement with theoretical predictions. The number of experimental results has been restricted, for the sake of keeping the readability of the figure rather than for an exhaustive search, but the literature provides a great number of high-quality papers and their values also nicely match the theoretical lines of the figure. We note that the  $A$ -plane related data match very well too. We also remark that the average blueshift of the three levels (due to the hydrostatic component of the strain field in this epilayer<sup>25</sup>) is nice evidence of a strong compression in the growth plane. This observation is confirmed by the observation of a small inten-

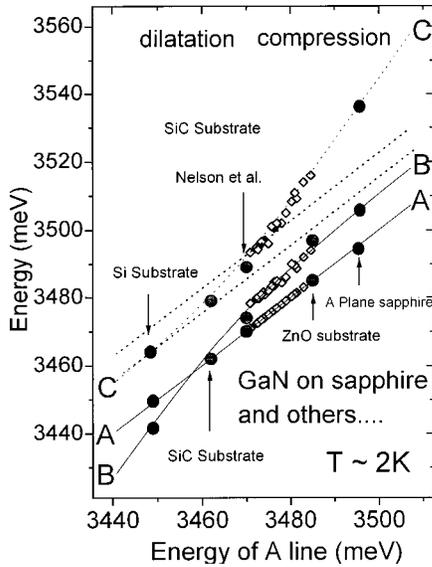


FIG. 5. Evolution of the transition energies in GaN epilayer grown with strain along the  $[0001]$  direction on various substrates: sapphire with GaN buffer layer (Ref. 12, open squares), SiC (a, Ref. 23; b, Ref. 24), Si (Ref. 22), ZnO (Ref. 21). Black circles on the right-hand side correspond to growth on  $A$ -plane sapphire. The literature locates the continuum of  $A$  in between the two bold dashed lines.

sity for the  $C$  line, compared to the intensities of the  $A$  and  $B$  ones. For epilayers that experience a strong biaxial compression in the  $\{0001\}$  plane, the intensity of the former is predicted to be much smaller than that of the latter, in reflectance experiments performed such that the electric field of the incident photon is perpendicular to the  $C$  axis of GaN.<sup>21</sup> This suggests a dominating contribution of the average in-plane deformation with respect to its anisotropy. If we now wish to consider the deformation potential issue, we have to write down the combined effects of the strain fields, crystal field splitting, and spin-orbit interaction on this sample. In order to obtain the three nonvanishing components of the strain in the GaN epilayer, it is convenient to assume that elasticity theory is still valid and to introduce an anisotropic stress tensor  $(\sigma_1, \sigma_2, 0, 0, 0, 0)$ , which represents the stress acting on the GaN due to the differences between its thermal expansion coefficients and those of the sapphire substrate. The symmetrized components of the strain tensor in the GaN epilayer are

$$e_{xx} + e_{yy} = e_{\perp} = (S_{11} + S_{12})(\sigma_1 + \sigma_2),$$

$$e_{zz} = S_{13}(\sigma_1 + \sigma_2),$$

$$e_{xx} - e_{yy} = (S_{11} - S_{12})(\sigma_1 - \sigma_2).$$

Neglecting excitonic effects, the problem is here reduced to the resolution of the following  $3 \times 3$  matrix in the basis of the three  $\Gamma_5$  functions of  $C_{2v}$  given by the compatibility relations with the  $\Gamma_9$  and  $\Gamma_7$  representations of  $C_{6v}$ :

$ \Gamma_5(X)\rangle$	$ \Gamma'_5(-iY)\rangle$	$ \Gamma''(Z)\rangle$
$\Delta_1 + \delta_1 + \delta_2 - \delta_3$	$\Delta_2$	$\Delta_3$
$\Delta_2$	$\Delta_1 + \delta_1 + \delta_2 + \delta_3$	$\Delta_3$
$\Delta_3$	$\Delta_3$	$\delta_1$

where the orbital components of the wave functions are indicated between parentheses, and where the strain-induced shifts are given as a function of the GaN deformation potentials  $\delta_1 = (D_1 + C_1)e_{zz} + (D_2 + C_2)e_{\perp} = a_1e_{zz} + a_2e_{\perp}$ ,  $\delta_2 = C_3e_{zz} + C_4e_{\perp}$ , and  $\delta_3 = C_5(e_{xx} - e_{yy})$ . From previous investigations of the strain effects on excitons in the case of  $\{0001\}$ -grown GaN epilayers, we obtained  $\Delta_1 = 10 \pm 0.1$  meV,  $\Delta_2 = 6.2 \pm 0.1$  meV, and  $\Delta_3 = 5.5 \pm 0.1$  meV. The values we take for the GaN deformation potentials are  $a_1 = -5.32$  eV,  $a_2 = -10.23$  eV, and  $C_3 = -2C_4 = -4.91$  eV.<sup>26</sup> And the strain versus stress relations are calculated using the following set of stiffness coefficients:  $C_{11} = 365$  GPa,  $C_{12} = 135$  GPa,  $C_{13} = 114$  GPa, and  $C_{33} = 381$  GPa.<sup>27</sup> It is interesting to note that we have three unknown quantities  $C_5$ ,  $\sigma_1$ , and  $\sigma_2$  together with three equations (the eigenvalues of the problem above), and three experimental values: the energies of the  $A$ ,  $B$ , and  $C$  lines. To help the numerical resolution of the problem, we note that the trace of the above matrix (the sum of experimental energies) is independent of  $C_5$ . Subtracting the zero-stress values previously calculated in Ref. 20, a straightforward calculation gives  $\sigma_1 + \sigma_2 = -2.438$  GPa. The oscillator strengths for line  $A$  in  $X[10-10]$ ,  $Y[-12-10]$ , and  $Z[0001]$  polarization are given by the square of the contributions of the three  $\Gamma_5$  eigenvec-

tors in the wave functions of the resolved problem. From Fig. 4, we note that the oscillator strengths are varying by a factor of 2 when the polarization is changed, which gives  $\Delta_2^2/\delta_3^2 \approx 8$ . The fitting of the data requires us to use  $C_5 = -2.4$  eV. Diagonalization of the  $3 \times 3$  matrix gives the following energies: 3496.4, 3507.5, and 3537.3 meV for *A*, *B*, and *C* lines, respectively. In terms of the oscillator strengths, the agreement between theory and experiment is illustrated in Fig. 4, where the variations of the oscillator strengths are plotted as a function the angle to the [10-10] direction. For the sake of completeness, the oscillator strength that we compute for line *C* is also given, but magnified by a factor 8. Values of  $\sigma_1$  and  $\sigma_2$  are  $-1.11$  and  $-1.32$  GPa, respectively. At last, the deformations along the [11-20] and [1-100] directions are

$$\varepsilon_{[11-20]} = (S_{11} + S_{13})(\sigma_1 + 3\sigma_2)/4 = -3.34 \times 10^{-3}$$

and

$$\varepsilon_{[1-100]} = (S_{11} + S_{13})(3\sigma_1 + \sigma_2)/4 = -3.07 \times 10^{-3}.$$

We note that the deformation in the direction parallel to the *c* axis of the sapphire substrate is the larger of the two, as

we expected  $\varepsilon_{[11-20]}/\varepsilon_{[1-100]} \approx 8.5/7.5$ , that is, the ratio between the sapphire thermal expansion coefficients.

In conclusion, reflectance spectroscopy performed in unpolarized and polarized light conditions on GaN grown onto *A*-plane sapphire has allowed us to measure accurately exciton binding energies of  $25 \pm 1$  meV for the *A* and *B* excitons. These values are similar to the values measured on GaN epilayers grown on conventional *C*-plane sapphire. This is consistent with the recent report of noticeable variations of the binding energy with strain in conventionally grown GaN epilayers,<sup>15</sup> the larger the biaxial compression (dilatation), the larger (smaller) the binding energy. The observation of these excited states is evidence of the possibility of growing high-quality GaN on *low symmetry* *A*-plane sapphire. At last, from the line-shape fitting of the reflectance structure taken for various in-plane polarizations, we could estimate the anisotropy of the built-in strain and we proposed the first estimation of the  $C_5$  deformation potential in GaN:  $-2.4$  eV.

The Groupe d'Etude des Semiconducteurs is "Unité Mixte de Recherche" 5650. Andenet Alemu acknowledges the Scientific Services of the French Embassy in Addis Abeba and the "Ministère des Affaires Etrangères" in Paris for financial support of his Ph.D. thesis.

- 
- <sup>1</sup>S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, New York, 1997).
- <sup>2</sup>T. Lei, K. F. Ludwig, and T. Moustakas, *J. Appl. Phys.* **74**, 4430 (1993).
- <sup>3</sup>S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, *Jpn. J. Phys.* **35**, L217 (1996).
- <sup>4</sup>B. Monemar, *Phys. Rev. B* **10**, 676 (1974).
- <sup>5</sup>T. Ogino and M. Aoki, *Jpn. J. Appl. Phys.* **19**, 2395 (1980).
- <sup>6</sup>M. Smith, G. D. Chen, J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, W. K. Kim, O. Aktas, A. Botchkarev, and H. Morkoç, *Appl. Phys. Lett.* **67**, 3387 (1995).
- <sup>7</sup>D. C. Reynolds, D. C. Look, W. Kim, O. Aktas, A. Botchkarev, A. Salvador, H. Morkoç, and D. N. Talwar, *J. Appl. Phys.* **80**, 594 (1996).
- <sup>8</sup>D. Volm, K. Oettinger, T. Streibl, D. Kovalev, M. Ben-Chorin, J. Diener, B. K. Meyer, J. Majewski, L. Eckey, A. Hoffmann, H. Amano, I. Akasaki, K. Hiramoto, and T. Detchprohm, *Phys. Rev. B* **53**, 16 543 (1996).
- <sup>9</sup>J. A. Freitas, Jr., K. Doverspike, and A. E. Wickenden, in *Gallium Nitride and Related Materials*, edited by R. D. Dupuis, J. A. Edmond, F. A. Ponce, and S. Nakamura, Materials Research Society Symposia Proceedings Vol. 395 (MRS, Pittsburgh, 1996), p. 485.
- <sup>10</sup>S. Chichibu, A. Shikanai, T. Azuhata, T. Sota, A. Kuramata, K. Horino, and S. Nakamura, *Appl. Phys. Lett.* **68**, 3766 (1996).
- <sup>11</sup>W. Shan, B. D. Little, A. J. Fischer, J. J. Song, B. Goldenberg, W. G. Perry, M. D. Bremser, and R. F. Davis, *Phys. Rev. B* **54**, 16 369 (1996).
- <sup>12</sup>M. Tchoukueu, O. Briot, B. Gil, J. P. Alexis, and R.-L. Aulombard, *J. Appl. Phys.* **80**, 5352 (1996).
- <sup>13</sup>A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, and S. Nakamura, *J. Appl. Phys.* **81**, 417 (1997).
- <sup>14</sup>B. J. Skromme, H. Zhao, B. Goldenberg, H. S. Kong, M. T. Leonard, G. E. Bulman, C. R. Abernathy, and S. J. Pearton, in *III-V Nitrides*, edited by I. Akasaki, B. Monemar, T. Moustakas, and F. Ponce, Materials Research Society Symposia Proceedings Vol. 449 (MRS, Pittsburgh, 1997), p. 713.
- <sup>15</sup>B. K. Meyer (Ref. 14), p. 497.
- <sup>16</sup>S. L. Chuang and C. S. Chang, *Semicond. Sci. Technol.* **12**, 252 (1997).
- <sup>17</sup>Yu. M. Sirenko, J. B. Leon, K. W. Kim, M. A. Littlejohn, and M. A. Stroscio, *Appl. Phys. Lett.* **69**, 2504 (1996).
- <sup>18</sup>M. Suzuki and T. Uenoyama, *Jpn. J. Appl. Phys., Part 2* **35**, L953 (1996).
- <sup>19</sup>B. Gil, S. Clur, and O. Briot, *Solid State Commun.* **104**, 267 (1997).
- <sup>20</sup>B. Gil, O. Briot, and R. L. Aulombard, *Phys. Rev. B* **52**, R17 028 (1995).
- <sup>21</sup>B. Gil, F. Hamdani, and H. Morkoç, *Phys. Rev. B* **54**, 7680 (1996).
- <sup>22</sup>S. Chichibu, T. Azuhata, T. Sota, H. Amano, and I. Akasaki, *Appl. Phys. Lett.* **70**, 2085 (1997).
- <sup>23</sup>D. K. Nelson, Yu. V. Melnik, A. V. Selkin, M. A. Yacobsen, V. A. Dmiriev, K. Irvine, and C. H. Carter, Jr., *Fiz. Tverd. Tela (Leningrad)* **38**, 651 (1996) [*Sov. Phys. Solid State* **38**, 455 (1996)].
- <sup>24</sup>S. N. Mohammad and H. Morkoç, in *Progress in Quantum Electronics*, edited by Marek Osinski (Elsevier, New York, 1995).
- <sup>25</sup>J. W. Orton, *Semicond. Sci. Technol.* **11**, 1026 (1996).
- <sup>26</sup>B. Gil and A. Alemu, *Phys. Rev. B* **56**, 12 446 (1997).
- <sup>27</sup>M. Yamaguchi, T. Yagi, T. Azuhata, T. Sota, K. Suzuki, S. Chichibu, and S. Nakamura, *J. Phys.: Condens. Matter* **9**, 241 (1997).