PHYSICAL REVIEW B VOLUME 60, NUMBER 16 15 OCTOBER 1999-II

Localization and anticrossing of electron levels in $GaAs_{1-x}N_x$ alloys

T. Mattila, Su-Huai Wei, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
(Received 17 May 1999)

The electronic structure in nitrogen-poor $GaAs_{1-x}N_x$ alloys is investigated using a plane-wave pseudopotential method and large supercells. Our calculations give a detailed description of the complex perturbation of the lowest conduction band states induced by nitrogen substitution in GaAs. The two principal physical effects are (i) a resonant impurity state $a_1(N)$ above the $a_1(\Gamma_{1c})$ conduction band minimum (important at ''impurity'' concentrations, $x\sim10^{17}$ cm^{-3}) and (ii) the creation of $a_1(L_{1c})$, and $a_1(X_{1c})$ states due to the splitting of the degenerate L_{1c} and X_{1c} GaAs levels (important at alloy concentrations, $x\sim1\%$ or $\sim10^{21}$ cm^{-3}). We show how the interaction of $a_1(N)$, $a_1(\Gamma_{1c})$, $a_1(L_{1c})$, and $a_1(X_{1c})$ provides a microscopic explanation for the origin of the experimentally observed anomalous alloy phenomena. [S0163-1829(99)50440-2]

Conventional III-V alloys such as $Ga_{1-x}In_xAs$ can be grown in a wide composition x range, and their electronic properties vary smoothly with composition. In contrast, mixed-anion nitride alloys such as $GaAs_{1-x}N_x$ can be grown in only narrow composition range near the endpoint constituents and exhibit anomalous composition dependent electronic properties.[1,2] Indeed, incorporation of even a small amount of the alloying species in the host induces dramatic changes in the electronic properties of $GaAs_{1-x}N_x$, both in the N-rich limit[1,2] and in the As-rich limit discussed here. Experiments on nitrogen in GaAs include early studies[3] on *impurity limit* ($x\sim10^{17}$ cm^{-3}) and more recent studies [4–9] on *alloys* ($x\sim1\%$ or $\sim10^{21}$ cm^{-3}):

In the nitrogen *impurity* limit, Hjalmarson *et al.*[10] predicted from a simple tight-binding model that nitrogen induces an *s*-like, nitrogen-localized resonance $a_1(N)$ *above* the delocalized conduction band minimum (CBM) $a_1(\Gamma_{1c})$. By applying pressure or alloying with GaP, the conduction band shifts rapidly upwards exposing this $a_1(N)$ state in the band gap.[3]

In the nitrogen *alloy* limit, luminescence,[4,5] electroreflectance,[6] and photomodulation[7] have shown unusual behavior of the two lowest interband transitions:

(i) The lowest-energy transition E_- shifts rapidly to the red as the nitrogen concentration is increased.[4–9] As pressure is applied,[7,8] this E_- transition shifts to the blue at a much slower rate than expected from the linear, concentration-weighted average of the pressure coefficients of the endpoint constituents GaAs and GaN. This pressure behavior is unusual, since in ordinary alloys[11] the pressure coefficient of the band gap is close to the average of the constituents. As pressure is further increased, the energy of E_- tends to saturate.[7] Magnetoluminescence measurements[12] have further shown that the electron effective-mass of E_- is about twice the value for CBM in GaAs, and that application of pressure can even further double this value. This contrasts sharply with ordinary III-V systems where the electron effective mass is pressure insensitive. Another striking peculiarity of the lowest-energy E_- transition is that the Γ_{1c}-X_{1c} crossover, seen in pure GaAs at a pressure of 4.3 GPa,[13] is not seen in $GaAs_{1-x}N_x$ alloys ($x\sim1\%$) even up to the highest pressure applied (~10 GPa).[7]

(ii) The higher energy transition E_+ shifts to the *blue* as the nitrogen concentration is increased.[6,7] As pressure is applied, the intensity of this initially weak transition increases[7] and its energy shifts to the blue at a rate similar to E_-. However, at high pressures the slope becomes large.[7]

Recently, Shan *et al.*[7] have noted that the experimental data on the alloys ($x\sim1\%$), including the splitting of the spectra into E_- and E_+ and the pressure saturation of E_- can be rationalized in terms of a two-level anticrossing model. Fitting the data to this two-level model explains the pressure data both naturally and successfully. However, since the data is fitted, the question is what is the microscopic identity of the two levels that enter such a model. Shan *et al.*[7] chose for these two levels the two lowest conduction states predicted by Hjalmarson *et al.*[10] for the *impurity limit*: the delocalized GaAs $a_1(\Gamma_{1c})$ CBM, and the nitrogen-induced defect level $a_1(N)$ that is above the CBM. This interpretation conflicts, however, with detailed band structure calculations,[14–17] which clearly show that in the ''alloy limit'' the lowest state E_- is *not* a delocalized $a_1(\Gamma_{1c})$-like state as assumed in the two-level model,[7,10] but rather a *nitrogen-localized state*.

In order to clarify the identity of the low-energy excitations in $GaAs_{1-x}N_x$, we have performed pseudopotential supercell calculations that are able to characterize the states that control the observed pressure and composition behavior. To model the experimental situation where nitrogen concentration is very small ($x\leqslant0.05-2\%$) one needs very large supercells ($\sim10^3$ atoms per cell) which is beyond the capability of currently available first-principles calculations. Because of this, and because of the well-known local density approximation (LDA) band gap error,[18] we adopt a different strategy: we fit an empirical pseudopotential to the *measured* band properties of GaAs and GaN, and to the *LDA calculated* GaAs/GaN valence band offset. To fit the band-edge pressure coefficients, we use a strain-dependent functional form of the pseudopotential.[19] The atomic positions in the supercell are determined by valence force field (VFF) model. The interatomic positions obtained by VFF and LDA in smaller supercells differ by less than 0.4%. In Table I we see that this pseudopotential indeed reproduces well the observed significant reduction of pressure coefficient[8,7] in the

TABLE I. The pressure derivatives of band-edge states in meV/GPa. The values calculated using the empirical pseudopotential method (EPM) are compared with the experimental values and with the values obtained using the first-principles linear augmented plane-wave method within local density approximation (LDA).

	$dE(\Gamma_{1c})/dp$	$dE(L_{1c})/dp$	$dE(X_{1c})/dp$	$dE(\Gamma_{15v})/dp$	$dE_{\rm gap}/dp$
	GaAs				
EPM	126	54	-19	14	112
LDA	114	52	-8	16	98
Expt.					106–122 [a]
	GaN				
EPM	29			−4	33
LDA	28			−3	31
Expt.					40 [b]
	$GaAs_{1-x}N_x$, $x=6.25\%$ (32 atom supercell)				
EPM	72			18	54
LDA	78			14	64
	$GaAs_{1-x}N_x$, $x=1.6\%$ (512 atom supercell)				
EPM	66			19	46
Expt.					51 [c]

[a]Reference 20.
[b]Reference 24.
[c]Reference 8 ($Ga_{0.92}In_{0.08}As_{0.985}N_{0.015}$).

low-nitrogen concentration $GaAs_{1-x}N_x$ alloy relative to GaAs. Crucial for the present application is accuracy in the position and pressure dependence of GaAs Γ_{1c}, L_{1c}, and X_{1c} states: Our method gives 0.32 (0.45) eV for the $\Gamma_{1c}-L_{1c}$ ($\Gamma_{1c}-X_{1c}$) separation, in good agreement with experiment.[20] Table I further shows that the LDA calculated pressure coefficients for the GaAs Γ_{1c}, L_{1c}, and X_{1c} states are well reproduced by the employed pseudopotential, and that the pressure dependence of the band gap is correctly divided into contributions from conduction and valence band edges as compared with LDA calculated values.

Figure 1 shows the behavior of the lowest conduction states as a function of x in $GaAs_{1-x}N_x$ alloy. To analyze the identity of the alloy states ψ_i we expand them in the Bloch states $\{\phi_{n,\mathbf{k}}\}$ of the underlying GaAs, and calculate[17] the spectral projection $\|A_{n,\mathbf{k}}\|^2$ given in Fig. 1 for Γ_{1c}, L_{1c}, and X_{1c} (in percentage). Our analysis reveals the following:

(i) $a_1(N)$ *state*: In the the *impurity* limit ($x\to 0$), nitrogen induces a resonant impurity state $a_1(N)$ inside the conduction band, just as envisioned by Hjalmarson *et al.*[10] We find that this state exhibits nitrogen localization: nearly half of the charge of the $a_1(N)$ state is contained inside the nearest-neighbor shell surrounding the nitrogen atom. This localization in real space is reflected in delocalization in reciprocal space, evidenced by the spectral projection (only 15 % is due to Γ). In the impurity limit ($Ga_{2048}As_{2047}N$, $x\sim 0.05\%$) we find this state to be 180 meV above the CBM, in good agreement with the experimental[3] estimate of 150–180 meV. However, as seen in Fig. 1, the energy of this $a_1(N)$ state rises rapidly as the nitrogen composition increases. Thus, in the alloy, which is the subject of all recent studies,[4–9] ($x\sim 1\%$) $a_1(N)$ is too far to act as a principal source for the low-energy anticrossing observed by Shan *et al.*[7] LDA calculations restricted to small supercells[12] cannot access the impurity concentrations, and therefore have missed the $a_1(N)$ state altogether.

(ii) *Perturbed host states:* Substitution of N on an As site exerts such a large perturbation that the host crystal states Γ_{1c}, L_{1c}, and X_{1c} mix thoroughly, forming new low-energy states. From the point of view of symmetry, substitution at a T_d symmetry site modifies the Γ_{1c} state $a_1(\Gamma_{1c})$, splits the fourfold L_{1c} valley into $a_1(L_{1c})$, and $t_2(L_{1c})$ representations, and splits the threefold X_{1c} valley into $a_1(X_{1c})$ and $e(X_{1c})$. All a_1-symmetric levels $a_1(N)$, $a_1(\Gamma_{1c})$, $a_1(L_{1c})$, and $a_1(X_{1c})$ can interact under the influence of the nitrogen potential, producing the low-energy states E_- and E_+.

(iii) E_- *state*: Our spectral analysis (Fig. 1) shows that at zero pressure the lowest conduction band E_- is mostly a combination of $a_1(\Gamma_{1c})$ and $a_1(L_{1c})$, with only little contribution from the higher energy $a_1(X_{1c})$ state. We see that in the alloy regime (right-hand side of Fig. 1) E_- is a significantly perturbed Γ_{1c} state and is thus very different from earlier models[7,10] which neglected the interaction of $a_1(\Gamma_{1c})$ with non-Γ states. Repulsion from these non-Γ a_1 states depresses E_-, leading to a pronounced redshift with composition (''optical bowing''). For $x\sim 1\%$, the energy of E_- shifts down by ~ 230 meV. This shows that the large band gap bowing observed[4–7,9] at small x is contributed mostly by the conduction band.[21] The $\Gamma_{1c}-L_{1c}$ interaction is apparent in our spectral projections, as seen in Fig. 1: E_- shows a reduced (increased) Γ_{1c} (L_{1c}) character as x increases. Since the L_{1c} electrons have heavier mass than the Γ_{1c} [for

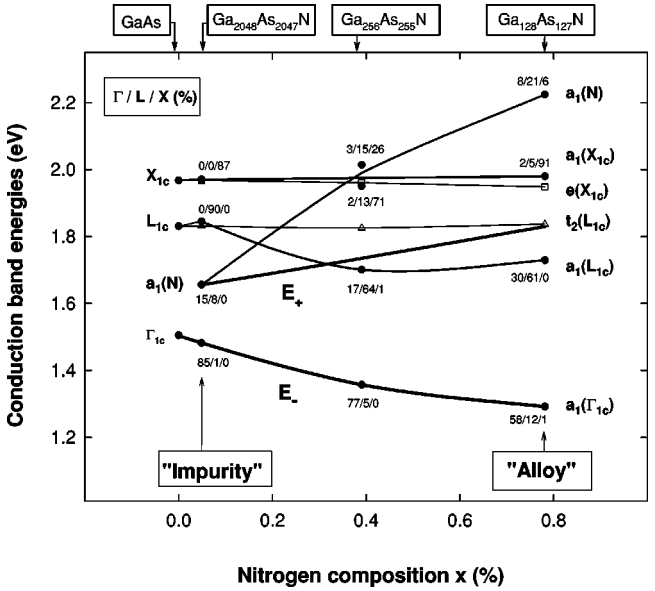

FIG. 1. The composition dependence of the energies of the lowest conduction band states in nitrogen-poor $GaAs_{1-x}N_x$ alloy. The percentage of Γ, L, and X character, respectively, for each state is shown. The thick solid lines illustrate the position of the E_- and E_+ transitions. The triply degenerate $t_2(L_{1c})$ state is depicted by open triangles, while the doubly degenerate $e(X_{1c})$ state is shown by open squares.

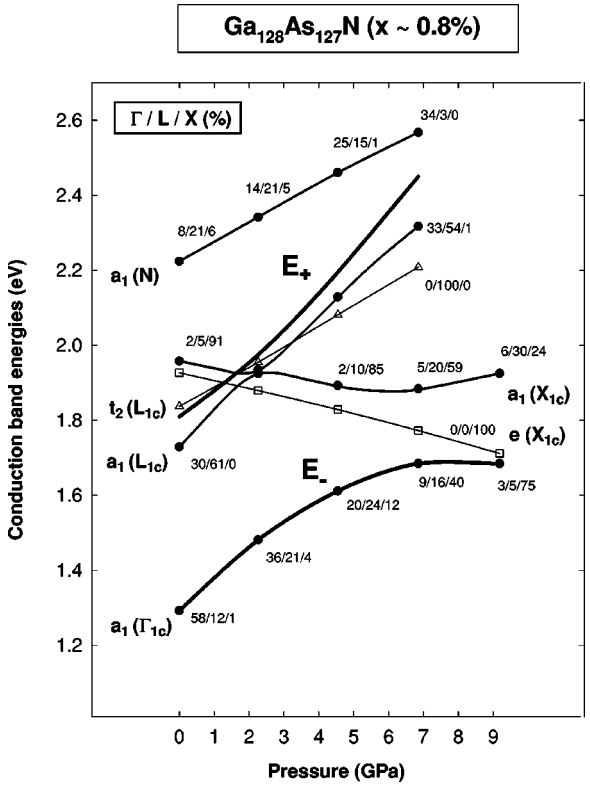

FIG. 2. The pressure dependence of the band-edge energies in $Ga_{128}As_{127}N$ ($x \sim 0.8\%$) alloy. The percentage of Γ, L, and X character for each state is shown. The thick solid lines illustrate the position of the experimentally observed E_- and E_+ transitions. The triply degenerate $t_2(L_{1c})$ state is depicted by open triangles, while the doubly degenerate $e(X_{1c})$ state is shown by open squares.

GaAs we find $m_e(\Gamma_{1c})=0.08$, $m_e^{\parallel}(L_{1c})=0.13$, $m_e^{\perp}(L_{1c})=1.51$], we find that nitrogen alloying increases the effective mass of the E_- state, in agreement with experimental observations.[12] This is in contrast with conventional alloys (e.g., InGaAs) where alloying does not promote significant $\Gamma-L$ mixing. The $\Gamma-L$ mixing (delocalization in reciprocal space) indicates localization in real space: Unlike conventional CBM states that are delocalized, the E_- state in $GaAs_{1-x}N_x$ alloy is localized (around the Ga atoms nearest to nitrogen). The localization suggests that electron diffusion lengths must be *intrinsically short* in $GaAs_{1-x}N_x$ alloy. However, despite the short-range localization around nitrogen sites, far away from nitrogen the E_- state has extended character. This long-range delocalization of E_- suggests a nonvanishing Hall mobility.

(iv) E_+ *state*: The E_+ state starts out at the nitrogen impurity ($x\rightarrow 0$) limit as an $a_1(N)$ impurity state, but as the nitrogen concentration increases, it acquires $a_1(L_{1c})$ character. At the impurity limit ($x\sim 0.05\%$) the coupling between $a_1(L_{1c})$ and $a_1(N)$ pushes the $a_1(L_{1c})$ energy above $t_2(L_{1c})$. However, this t_2-a_1 splitting remains small (13 meV). When the nitrogen concentration increases, the energy of the resonant state $a_1(N)$ increases rapidly, and its coupling with $a_1(L_{1c})$ leads to the lowering of the energy of $a_1(L_{1c})$. Figure 1 shows that $a_1(L_{1c})$ remains dominantly L-like ($90\%\rightarrow 61\%$) with increasing Γ character ($0\%\rightarrow 30\%$) as x is increased. While $a_1(L_{1c})$ exhibits a weak localization around nitrogen at the impurity limit, at larger concentrations this state becomes more delocalized as evidenced by the higher Γ content.

(v) *Transition probabilities*: We find that the dipole transition matrix element $I=\langle\psi_i|\hat{p}|\psi_{VBM}\rangle^2$ from conduction state i to the VBM, is directly proportional to the percentage of the Γ character of the conduction state i. Therefore, in Fig. 1 we see that in the ''alloy'' regime there are three levels that could serve as a transition source to VBM: $a_1(\Gamma_{1c})$, $a_1(L_{1c})$, and $a_1(N)$. However, our calculations show that the position of $a_1(\Gamma_{1c})$ is not sensitive to the configuration of nitrogen atoms in the supercell, while the relative position of $a_1(N)$ and $a_1(L_{1c})$ varies strongly depending on the position of nitrogen atoms in the anion sublattice. Therefore, we suggest that while the E_- transition originates from a single state formed by hybridization of $a_1(\Gamma_{1c})$ and $a_1(L_{1c})$ (shown by the thick solid line), the observed E_+ transition originates from a configuration weighted average of the $a_1(N)$ and $a_1(L_{1c})$ levels. In Fig. 1 we estimate the position of E_+ (shown as upper thick solid line) as a weighted average of the two levels based on their Γ character. Note that when $a_1(N)$ and $a_1(L_{1c})$ are far apart in energy, this estimate tends to overestimate the position of E_+. We find that with increased nitrogen content the *increase* in E_+ is linear and nearly equal to the decrease in E_-, in agreement with experiment.[6]

(vi) *Pressure effects*: Figure 2 shows the calculated band-edge energies as a function of pressure in $Ga_{128}As_{127}N$ ($x\sim 0.8\%$). It also shows the Γ, L, and X character of each state as a function of pressure. We observe the following.

(a) As pressure increases, the E_- state experiences repulsion from two sources. Initially, the $\Gamma(L)$ character of E_-

state decreases (increases) due to the anticrossing with $a_1(L_{1c})$ and $a_1(N)$. At higher pressures, the $\Gamma-L$ interaction becomes less important and is replaced by repulsion from the $a_1(X_{1c})$ state, as evidenced by the rapidly increasing X character of the E_- state. The pressure coefficient of the transition between E_- and the VBM starts from 63 meV/GPa at $p=0$ and declines to less than 10 meV/GPa as the pressure increases to >5 GPa,[22] thus reproducing the experimental observations.[7] Since the electron effective mass at X_{1c} is considerably larger than at Γ_{1c} [for GaAs, we find $m_e(\Gamma_{1c})=0.08$, $m_e^{\parallel}(X_{1c})=0.25$, $m_e^{\perp}(X_{1c})=1.80$], the mixing of X_{1c} character into E_- results in a significant increase in $m^*(E_-)$ as a function of pressure, as seen in experiments.[12]

(b) As pressure is applied, both $a_1(N)$ and $a_1(L_{1c})$ shift nearly linearly up in energy. The pressure coefficient for their Γ-weighted average E_+ has a small value of 60 meV/GPa at small pressures (similar to E_-) but increases to a value ~ 100 meV/GPa at higher pressure. We further note that at small nitrogen concentrations (''impurity limit'') the pressure dependence of $a_1(N)$ is similar to E_+ shown in Fig. 2. This result provides a successful explanation for the experimental pressure data by Wolford *et al.*[3]

(c) As pressure is applied, the transition probability (reflected by the Γ character) for E_- decreases while that for E_+ increases. Thus, while E_- is the dominating transition at low pressures, this role is shifted to E_+ at high pressures, in agreement with the experimental observations.[7]

(d) $\Gamma-X$ crossing in bulk GaAs at 4.3 GPa,[13] does not occur in $GaAs_{1-x}N_x$ alloy due to two reasons: First the increased separation of E_- to $a_1(X_{1c})$ at $p=0$ and second the reduced pressure coefficient of the E_- state [repulsion from $a_1(X_{1c})$ and $a_1(L_{1c})$ states].

In summary, we find that nitrogen substitution in GaAs leads to a complex perturbation of the lowest conduction band states. Our calculations provide a detailed explanation for the microscopic origin of the numerous anomalous experimental observations in $GaAs_{1-x}N_x$ alloys.

This work was supported by the U.S. Department of Energy, OER-BES-DMS Grant No. DE-AC36-98-GO10337.

[1] L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. B **54**, 17 568 (1996).

[2] T. Mattila and A. Zunger, Phys. Rev. B **58**, 1367 (1998).

[3] D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, in *Physics of Semiconductors*, edited by D. J. Chadi and W. A. Harrison (Springer, New York, 1984), p. 627.

[4] M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, Jpn. J. Appl. Phys., Part 2 **33**, L1056 (1992).

[5] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).

[6] J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 3312 (1999).

[7] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).

[8] P. Perlin, S. G. Subramanya, D. E. Mars, J. Kruger, N. A. Shapiro, H. Siegle, and E. R. Weber, Appl. Phys. Lett. **73**, 3703 (1998).

[9] G. Pozina, I. Ivanov, B. Monemar, J. V. Thordson, and T. G. Andersson, J. Appl. Phys. **84**, 3830 (1998).

[10] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[11] S. Adachi, J. Appl. Phys. **58**, R1 (1985).

[12] E. D. Jones, N. A. Modine, A. A. Allerman, S. R. Kurtz, A. F. Wright, S. T. Tozer, and X. Wei, Phys. Rev. B **60**, 4430 (1999).

[13] S. Ernst, A. Goni, K. Syassen, and M. Cardona, Phys. Rev. B **53**, 1287 (1996).

[14] A. Rubio and M. L. Cohen, Phys. Rev. B **51**, 4343 (1995).

[15] J. Neugebauer and C. G. Van de Walle, Phys. Rev. B **51**, 10 568 (1995).

[16] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).

[17] L.-W. Wang, L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **80**, 4725 (1998).

[18] A. Zunger and A. J. Freeman, Phys. Rev. B **17**, 4850 (1977).

[19] T. Mattila, L.-W. Wang, and A. Zunger, Phys. Rev. B **59**, 15 270 (1999). The parameters of our pseudopotential can be found in http://www.sst.nrel.gov/data/GaAsNepm.html.

[20] *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 22, Pt. a (Springer, Berlin, 1987).

[21] The VBM energy is shifted up by 25 meV at $x\sim 1\%$, contributing about 20% to band gap bowing parameter $b(x)$. This is a large contribution, reflecting the fact that GaN VBM is 2.2 eV lower in energy than GaAs VBM (Ref. 23).

[22] Note that not all of the reduction of the pressure coefficient at high pressures is due to alloying effect. Indeed, even for a pure semiconductor, a_p decreases as pressure increases: Our LDA calculated band gap of pure GaAs as a function of the volume logarithm $\ln V$ as well as a function of pressure p show that the slope $dE_{gap}/d\ln V$ is nearly a constant. However, since $a_p = dE_{gap}/dp = (1/B)dE_{gap}/d\ln V$, and since the bulk modulus B increases with pressure, the slope $a_p = dE_{gap}/dp$ decreases as a function of p.

[23] S.-H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[24] T. Suski, P. Perlin, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, M. Bockowski, and S. Porowski, Appl. Phys. Lett. **67**, 2188 (1995).