Interface-related exciton-energy blueshift in $GaN/Al_xGa_{1-x}N$ zinc-blende and wurtzite single quantum wells

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The role of nonabrupt interfaces on the confined exciton energy blueshift in zinc-blende and wurtzite $GaN/Al_xGa_{1-x}N$ single quantum wells (QWs) is investigated. The theoretical calculations are performed taking into account a range of values for the electron and heavy-hole effective masses in both phases, which is compatible to those that have been measured and/or estimated from first principles calculations. The interface related ground state exciton energy blueshift is shown to depend strongly on the nonabrupt interfaces widths in the case of thin QWs ($\lesssim$80 Å), being a little higher in zinc-blende than in similar wurtzite QWs. For a 50 Å (80 Å) wide $GaN/Al_{0.3}Ga_{0.7}N$ single QW whose nonabrupt interfaces have a thickness of 10 Å, the nonabrupt interface related ground state exciton energy blueshift is 26 meV (5 meV) and 19 meV (3 meV) in the zinc-blende and wurtzite phases, respectively. It is shown the impossibility of the sharp interface picture to describe exciton related emission properties of $GaN/Al_xGa_{1-x}N$ single QWs with a precision better than 10 meV. [S0163-1829(99)02532-1]

I. INTRODUCTION

Recent research interest in GaN and AlN based quantum wells (QWs) is driven by their blue-green light emission properties, which find technological applications in light-emitting diodes and lasers.[1] Since sapphire substrates presented many advantages in the growth process, most of early $GaN/Al_xGa_{1-x}N$ QWs were grown in the wurtzite phase.[2–10] However, there is an increasing interest nowadays in zinc-blende $GaN/Al_xGa_{1-x}N$ QWs due to the improvement of their growth processes to take advantage of the higher GaN saturated electron drift velocity, easy cleavage, and lower band energy in technological applications.[11–22] Despite several measurements and electronic structure calculations, the uncertainty in the values of some important parameters for both wurtzite and zinc-blende GaN and AlN is still important. This is the case of the electron and hole effective masses, for example, for which a relatively large range of values were considered in the literature.[23–38] This range of values is due to the samples quality used in the experiments, as well as the differences and/or the improvement in the GaN and AlN band structure calculations performed with first principles methods. The interfaces quality in wurtzite and zinc-blende $GaN/Al_xGa_{1-x}N$ QWs is also not clear since results on their heterointerfaces characterization continue to be very limited. Meanwhile, interface effects should be very important in $GaN/Al_xGa_{1-x}N$ QWs because they can strongly change their confinement properties. It is well known, for example, the important role of the interfaces on the optical properties of $GaAs/Al_xGa_{1-x}As$ QWs, see the revision paper on this subject by Herman, Bimberg, and Christen.[39] Since for the same Al molar fraction content the confinement depth in $GaN/Al_xGa_{1-x}N$ QWs is stronger than in $GaAs/Al_xGa_{1-x}As$ QWs, interface effects should be more important in the former than in the latter.

Although most of the early experiments on the optical transitions in $GaN/Al_xGa_{1-x}N$ QWs resorted to a quantum confinement picture (and then confined QW excitons) for their description (see Khan *et al.*,[2] for example), the optical emission mechanism in $GaN/Al_xGa_{1-x}N$ QWs is a matter of controversy nowadays.[40] Confined excitons seem to have an important role,[41] but localized and trap states related to compositional fluctuations are also relevant.[42–44] To the knowledge of the authors, formal theoretical calculations on the exciton energy in GaN/AlGaN QWs were published only recently, being restricted to the wurtzite phase and totally disregarding interface effects.[45,46] Chung and Chang[45] have investigated the effects of well width and Al molar fraction in the barriers regions on the exciton peak and binding energy in wurtzite $GaN/Al_xGa_{1-x}N$ QWs. They performed calculations within the effective mass approximation using heavy-hole effective masses 0.27 and $0.30m_0$ (m_0 is the free space electron mass) for the GaN and $Al_{0.2}Ga_{0.8}N$ layers, respectively. Through a variational technique in the momentum space, Chung and Chang[45] have obtained for large QWs a confined exciton binding energy about 18 meV, which is 8 meV lower than the most recently published data on the bulk GaN exciton energy ($\sim$26 meV).[47–49] However, using a hole effective mass of about $1.1m_0$ along the *c*-axis direction (m_0 is the free electron mass), they found a larger bulk value (around 25 meV) for the exciton binding energy, which is very close to the bulk GaN exciton energy. In both cases, Chung and Chang[45] argue to have obtained good agreement of their theoretical calculations with available experimental data (only seven points collected from three experiments) for QWs of several widths and aluminum molar content in the $Al_xGa_{1-x}N$ barriers. Bigenwald *et al.*[46] performed a careful study of the electronic and optical properties of wurtzite $GaN/Al_{0.3}Ga_{0.7}N$ QWs in the context of a six-band envelope function approach, obtaining a large well limit behavior for the confined exciton binding energy close to 26 meV, but a much higher exciton binding energy for shorter well widths

in comparison to the results of Chung and Chang.[45]

Nonabrupt interfaces should occur in actual wurtzite and zinc-blende $GaN/Al_xGa_{1-x}N$ QW samples, at least as a consequence of the chemical potential difference between GaN-$Al_xGa_{1-x}N$ heterojunctions.[50] However, all previous theoretical calculations concerning $GaN/Al_xGa_{1-x}N$ QWs have addressed to ideal semiconductor interfaces, and thus the confinement potential was always described within a sharp interface picture. Recently, a blueshift in the photoluminescense spectra due to quantum well thickness fluctuations and a graded interface related GaN phonon mode broadening have been observed, the former with a time-resolved photoluminescence experiment,[8] and the latter through a resonant Raman scattering experiment.[9] These results indicate the need to obtain information concerning nonabrupt interface effects in GaN and AlN based heterostructures.

A theoretical investigation is performed in this work on the role of nonabrupt interfaces in the exciton energy blueshift in $GaN/Al_xGa_{1-x}N$ zinc-blende and wurtzite single QWs. The $GaN/Al_xGa_{1-x}N$ nonabrupt interface description is an adaptation of the framework that Freire, Farias, and co-workers[51] have used to study nonabrupt interface effects in $GaAs/Al_xGa_{1-x}As$ heterostructures within the effective mass approximation. The confined exciton energy is obtained following a variational approach. The aluminum molar fraction x is limited to be smaller than 0.43 to avoid Γ and X band mixing effects in the zinc-blende QW calculations.[30] The uncertainty in the electron and heavy-hole effective mass values[23–38] on the exciton energy is taken into account by considering fluctuations ($\pm 15\%$ in the case of electrons, $\pm 30\%$ in the case of heavy holes) around specific values, which have been selected among the published data.[23,35] Considering that actual $GaN/Al_xGa_{1-x}N$ zinc-blende and wurtzite single QW samples have nonabrupt interfaces, an analysis of the results presented in this work allows us to highlight the impossibility of the sharp interface picture to describe the ground state exciton energy in 50 Å (80 Å) wide $GaN/Al_{0.3}Ga_{0.7}N$ zinc-blende and wurtzite actual single QW samples with a precision better than 26 meV (5 meV) for the former, and 19 meV (3 meV) for the latter.

This work is organized as follows. In Sec. II, a description of the $GaN/Al_xGa_{1-x}N$ QW model which considers the existence of nonabrupt interfaces is presented. Results and discussions on the interface related exciton energy blueshift in $GaN/Al_xGa_{1-x}N$ zinc-blende and wurtzite single QWs are described in Sec. III. Concluding remarks close this work in Sec. IV.

II. $GaN/Al_xGa_{1-x}N$ QUANTUM WELL MODEL AND EQUATIONS

The light emission peaks due to confined excitons in $GaN/Al_xGa_{1-x}N$ single QWs are shifted towards high energy in comparison to those associated with the GaN confining layers.[2] This blueshift can be of several tenths of meV, depending on the quantum wells width and confinement depth. To investigate the role of nonabrupt interfaces on the blueshift of the ground state electron-heavy-hole (e-h) exciton energy peaks, the $GaN/Al_xGa_{1-x}N$ single QWs are described in here within the framework of the effective-mass approximation considering the following Hamiltonian in cylindrical coordinates:[52]

$$H = -\frac{\hbar^2}{2\mu_{e-h}}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right]-\frac{\hbar^2}{2}\frac{\partial}{\partial z_e}\left[\frac{1}{m_e^{\perp}(z_e)}\right]\frac{\partial}{\partial z_e} - \frac{\hbar^2}{2}\frac{\partial}{\partial z_h}\left[\frac{1}{m_h^{\perp}(z_h)}\right]\frac{\partial}{\partial z_h}+V_e(z_e)+V_h(z_h) - \frac{e^2}{\epsilon[\rho^2+(z_e-z_h)^2]^{1/2}}, \quad (1)$$

where ρ, ϕ, and z_α ($\alpha=e$ for electrons and $\alpha=h$ for heavy holes) are the relative electron-heavy-hole cylindrical system coordinates, $m_e^{\perp}(z_e)$ and $m_h^{\perp}(z_h)$ are the electron and heavy-hole effective mass perpendicular to the grown planes of the [001] and [0001] oriented $GaN/Al_xGa_{1-x}N$ zinc-blende and wurtzite single QWs, respectively, $\epsilon=9.5$ is the GaN dielectric constant[6,47,48,53] $\mu_{e\text{-}h}=m_e^{\parallel}m_h^{\parallel}/(m_e^{\parallel}+m_h^{\parallel})$ is the reduced mass of the electron-heavy-hole pair, and $V_\alpha(z_\alpha)$ is the graded quantum confinement potential for the α-type carrier, whose expressions are given later [see Eq. (4)].

In both zinc-blende and wurtzite phases, GaN has a direct gap at the axis passing through the Γ-symmetry point and AlN has an indirect gap at the axis passing through the Γ- to X-symmetry points.[29,30,34] The compound alloy $Al_xGa_{1-x}N$ presents a direct to an indirect $\Gamma \rightarrow X$ gap transition when $x > 0.43$ (Ref. 30), $x > 0.57$ (Ref. 34) in the zinc-blende phase. The bowing dependence of the $Al_xGa_{1-x}N$ gap energy (in eV) on x is given by[30,54–60]

$$E_{g,Al_xGa_{1-x}N}(x) = (1-x)E_{g,GaN}+xE_{g,AlN}+bx(x-1), \quad (2)$$

where b is bowing coefficient, which is equal to 0.53 eV for the zinc-blende phase[55] and 1.0 eV for the wurtzite phase;[57–60] $E_{g,Al_xGa_{1-x}N}$, $E_{g,GaN}$, and $E_{g,AlN}$ are the $Al_xGa_{1-x}N$, GaN, and AlN gap energy in the axis which passes through the Γ point, respectively (see Table I).[14,18,19,29,35,61–65]

TABLE I. Zinc-blende and wurtzite GaN,AlN gap energies and electron and heavy-hole effective masses in the Γ point at low temperatures. m_0 is the free space electron mass.

Sample	E_g^{Γ}(eV)	$m_e^{\perp}(m_e^{\parallel})/m_0$	$m_h^{\perp}(m_h^{\parallel})/m_0$
GaN zinc blende	3.30	0.19 (0.19)	0.86 (2.00)
AlN zinc blende	6.00	0.33 (0.33)	1.43 (4.55)
GaN wurtzite	3.50	0.19 (0.19)	2.00 (2.04)
AlN wurtzite	6.28	0.35 (0.35)	3.53 (11.14)

To the knowledge of the authors, no experimental result has been published up to now concerning the dependence of the electron and heavy-hole masses on the aluminum molar fraction in the $Al_xGa_{1-x}N$ alloy [$m_{\alpha,Al_xGa_{1-x}N}^{\perp}(x)$, $\alpha=e$ for electrons and $\alpha=h$ for heavy holes]. In this work, contributions to this dependence due x^2 terms are disregarded, which

means that the electron and heavy-hole masses $m^{\perp}_{\alpha,\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}}(x)$ in the Γ point are related to $m^{\perp}_{\alpha,\mathrm{GaN}}$ and $m^{\perp}_{\alpha,\mathrm{AlN}}$ through the following linear relation:

$$m^{\perp}_{\alpha,\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}}(x)=(1-x)m^{\perp}_{\alpha,\mathrm{GaN}}+xm^{\perp}_{\alpha,\mathrm{AlN}}. \tag{3}$$

Mirrored on the interface description framework that Freire, Farias, and co-workers[51] have used to study nonabrupt GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}$As heterostructures, it is assumed that the expressions for $E_{g,\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}}$ and $m^{\perp}_{\alpha,\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}}(x)$ are valid for very thin samples, i.e., few monolayers wide $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ films. Consequently, the replacement of x by a function of z, $x\rightarrow y(z)$, in Eqs. (2) and (3) turns out to be possible. This replacement allows to obtain the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ gap energy as well as the electron and heavy-hole masses in term of $y(z)$, which is very useful for the description of nonabrupt GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ interfaces. Assuming that the spatial variation of the aluminum molar fraction $y(z)$ changes linearly from $x\rightarrow 0$ $(0\rightarrow x)$ in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$-GaN (GaN-$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$) interface, the graded potentials $V_\alpha(z_\alpha)$ (in eV) and the effective masses $m^{\perp}_{\alpha}(z_\alpha)$ describing the carriers confinement in a nonabrupt GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ single QW within the effective mass approximation, are given by

$$V_\alpha(z_\alpha)/Q_\alpha=\begin{cases}0, & |z_\alpha|<w_a/2-w\\ [E_{g,\mathrm{AlN}}-E_{g,\mathrm{GaN}}-b]y(z_\alpha)+by^2(z_\alpha), & w_a/2-w<|z_\alpha|<w_a/2,\\ [E_{g,\mathrm{AlN}}-E_{g,\mathrm{GaN}}-b]x+bx^2, & |z_\alpha|>w_a/2,\end{cases} \tag{4}$$

$$m^{\perp}{}_{\alpha}(z_\alpha)/m_0=\begin{cases}m^{\perp}_{\alpha,\mathrm{GaN}}, & |z_\alpha|<w_a/2-w,\\ m^{\perp}_{\alpha,\mathrm{GaN}}+[m^{\perp}_{\alpha,\mathrm{AlN}}-m^{\perp}_{\alpha,\mathrm{GaN}}]y(z_\alpha), & w_a/2-w<|z_\alpha|<w_a/2,\\ m^{\perp}_{\alpha,\mathrm{GaN}}+[m^{\perp}_{\alpha,\mathrm{AlN}}-m^{\perp}_{\mathrm{GaN}}]x, & |z_\alpha|>w_a/2,\end{cases} \tag{5}$$

where $y(z_\alpha)=x(|z_\alpha|-w_a/2+w)/w$, Q_α is the band offset for the α-type carrier, which is considered to be $Q_e:Q_h=70:30$ in this work,[4,5,7,8,45,46,54] w is the width of the symmetrical nonabrupt interfaces and w_a is the width of the abrupt QWs, and m_0 is the free space electron mass.

Since an analytical solution of the Schrödinger equation for the Hamiltonian describing the nonabrupt GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ single QW [see Eq. (1)] is not possible, a variational approach solution is resorted. By disregarding the electron-heavy-hole interaction, the following two independent equations (one for each type of carrier) are obtained:

$$\left\{\frac{\hbar^2}{2}\frac{\partial}{\partial z_\alpha}\left[\frac{1}{m^{\perp}_{\alpha}(z_\alpha)}\right]\frac{\partial}{\partial z_\alpha}+V_\alpha(z_\alpha)\right\}\psi_\alpha(z_\alpha)=E_\alpha\psi_\alpha(z_\alpha), \tag{6}$$

where ψ_α is the wave function for the α-type carrier, which can be calculated (together with the carriers energy levels E_α) through the scheme of Ando and Itoh[66] to solve Eq. (6) numerically.

Restricting the interest to ground state excitons in nonabrupt GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ single QWs, in a variational approach the following trial wave function for the carriers ground state can be used to calculate approximately the ground state exciton binding energy $E_b(w_a,w)$ in nonabrupt GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ single QWs:

$$\Psi(z_e,z_h,\rho)=\psi_e(z_e)\psi_h(z_h)\psi_{e-h}(\rho), \tag{7}$$

with

$$\psi_{e-h}(\rho)=\left(\frac{2}{\pi\lambda^2}\right)^{1/2}\exp(-\rho/\lambda), \tag{8}$$

and where λ is the variational parameter. In this case, $E_b(w_a,w)$ is given by

$$E_b(w_a,w)=-\min_{\lambda}\langle\Psi(z_e,z_h,\rho)|H|\Psi(z_e,z_h,\rho)\rangle. \tag{9}$$

Then, the ground state exciton energy $E_{\mathrm{ex}}(w_a,w)$ as a function of the GaN/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ single QW width w_a and interfaces thickness w is

$$E_{\mathrm{ex}}(w_a,w)=E_{g,\mathrm{GaN}}+E_e(w_a,w)+E_h(w_a,w)-E_b(w_a,w), \tag{10}$$

where $E_e(w_a,w)$ and $E_h(w_a,w)$ are, respectively, the electron and heavy-hole ground state energy in the nonabrupt QW, which are obtained from the numerical solution of Eq. (6). While the lattice constants and gap energy of the zinc-blende and wurtzite GaN and AlN phases are well established, this is not the case for their electron and heavy-hole masses. In the range of measured and first principles estimated values for them,[23–38] Table I presents those which seems to be the best choice nowadays.[35] To investigate the effect of the carrier effective masses range of values on the ground state exciton energy, results are also obtained considering a $\pm 15\%$ $(\pm 30\%)$ variation of the electron (heavy-hole) mass in both the GaN and AlN phases. The difference on the range of values for the electron and heavy-hole masses is a consequence of the difficulty in measuring and/or calculating (better to say estimating) them with first principles methods.

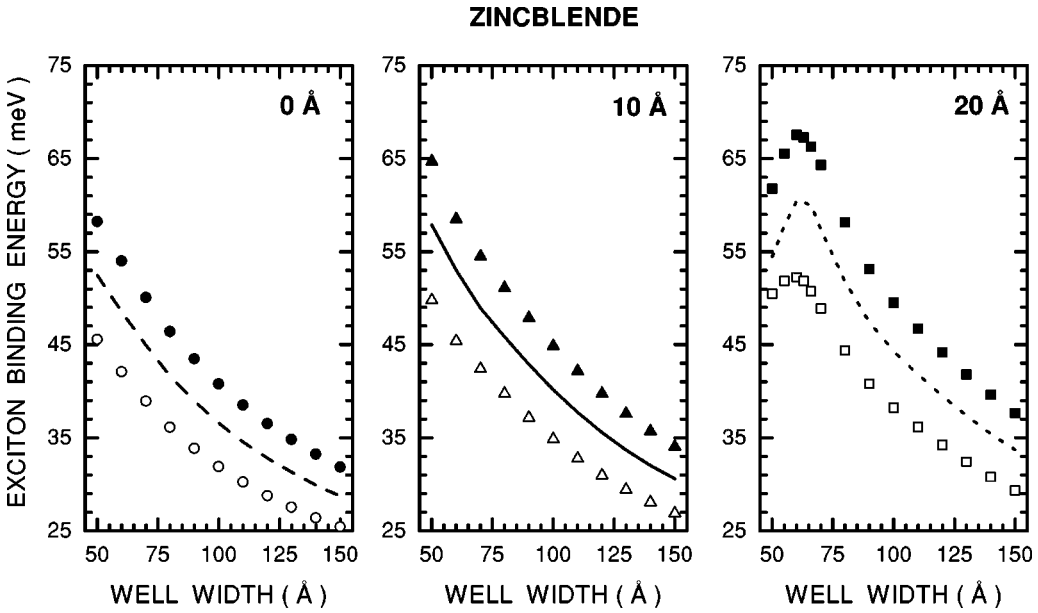

FIG. 1. The well width dependence of the ground state exciton binding energy $E_b(w_a,w)$ in zinc-blende GaN/$Al_{0.3}Ga_{0.7}N$ single QWs with abrupt interfaces (left panel), 10 Å (central panel), and 20 Å (right panel) wide interfaces. The results depicted with long dashed, solid, and dotted lines were obtained considering the gap energy and the carriers effective masses given in Table I. The black circles, triangles, and squares show the ground state exciton binding energy $E_b(w_a,w)$ calculated considering that the electron and heavy-hole masses are, respectively, +15 and +30 % heavier than those in Table I. The open circles, triangles, and squares show the ground state exciton binding energy E_b calculated considering that the electron and heavy-hole masses are, respectively, −15 and −30 % lighter than those in Table I.

III. THE INTERFACE RELATED EXCITON ENERGY BLUESHIFT

The existence of nonabrupt interfaces changes the wave function $\Psi(z_e,z_h,\rho)$ spreading into the $Al_xGa_{1-x}N$ barrier regions, and shifts the confined electron and heavy-hole energy levels toward higher energies. The resulting increase on the confinement degree due to the nonabrupt interfaces enhances carriers localization in the central region of the GaN/$Al_xGa_{1-x}N$ single QWs, blueshifting the exciton binding energy $E_b(w_a,w)$. This behavior is clearly shown in Fig. 1 and Fig. 2 for zinc-blende and wurtzite GaN/$Al_{0.3}Ga_{0.7}N$ single QWs, respectively. In these figures, one can observe the variation of the exciton binding energy with the well width w_a when the interface width is 0 Å (sharp well, left panel), 10 Å (nonabrupt well, central panel) and 20 Å (nonabrupt well, right panel). The exciton energies in these QWs calculated using the data given in Table I are depicted as long dashed, solid and dotted lines in Fig. 1 and Fig. 2, while those obtained considering a variation of +15 and +30 % (−15 and −30 %), respectively, on the electron and heavy-hole mass in both GaN and AlN are represented by black (open) circles, triangles, and squares. Consequently, all the possible range of values for the exciton binding energy that can be obtained as a consequence of an imprecise knowledge concerning the electron and heavy-hole masses are located in the region between the black and open symbols. Any experimental data on GaN/$Al_{0.3}Ga_{0.7}N$ single QW confined related exciton binding energies should be localized in the region between the black and open symbols if the electron and heavy-hole masses in the samples are in the range of values considered here.

According to the assumption the actual nonabrupt interface thickness does not change if the same process is used for growth of GaN/$Al_xGa_{1-x}N$ single QWs of several widths,[67] the nonabrupt interface effects become less important when the well is larger. Consequently, the nonabrupt interface related exciton binding energy $E_b(w_a,w)$ shift towards higher energies is smaller when the QWs are wider. For the same well and interface width, the exciton binding energy is always a little higher in the wurtzite than in the zinc-blende QWs, which can be observed comparing Fig. 1 to Fig. 2. The two-dimensional (2D) exciton binding energy should decrease when the well is thin enough (see, for example, classical papers[52] on confined excitons in GaAs/$Al_xGa_{1-x}As$ QWs), approaching asymptotically to the three-dimensional exciton binding energy value of the semiconductor type in the barriers. On the other hand, when the well is wide enough, the two-dimensional exciton binding energy should decrease continuously, approaching asymptotically to the three-dimensional exciton binding energy value of the semiconductor type in the well. In both Figs. 1 and 2, it is clear that the very thin well asymptotic behavior should occur in GaN/$Al_{0.3}Ga_{0.7}N$ single QWs only when their widths are smaller than 50 Å. However, the existence of wide enough interfaces can anticipate the asymptotic approach to the 3D $Al_{0.3}Ga_{0.7}N$ exciton binding energy since it reduces the mean width of the confinement QW—this behavior is clearly shown in the right panels of Figs. 1 and 2. In the wide well behavior case, the exciton binding energy in zinc-blende and wurtzite GaN/$Al_{0.3}Ga_{0.7}N$ single QWs calculated in this work approaches asymptotically the bulk GaN exciton binding energy $E_{b(3D)}$, which is 26 meV in both the zinc-blende and wurtzite phases,[68] a result that is in very good agreement with recent experimental data.[47–49]

Although the interface related energy shifts on the ground state exciton binding energy $E_b(w_a,w)$ due to carriers con-

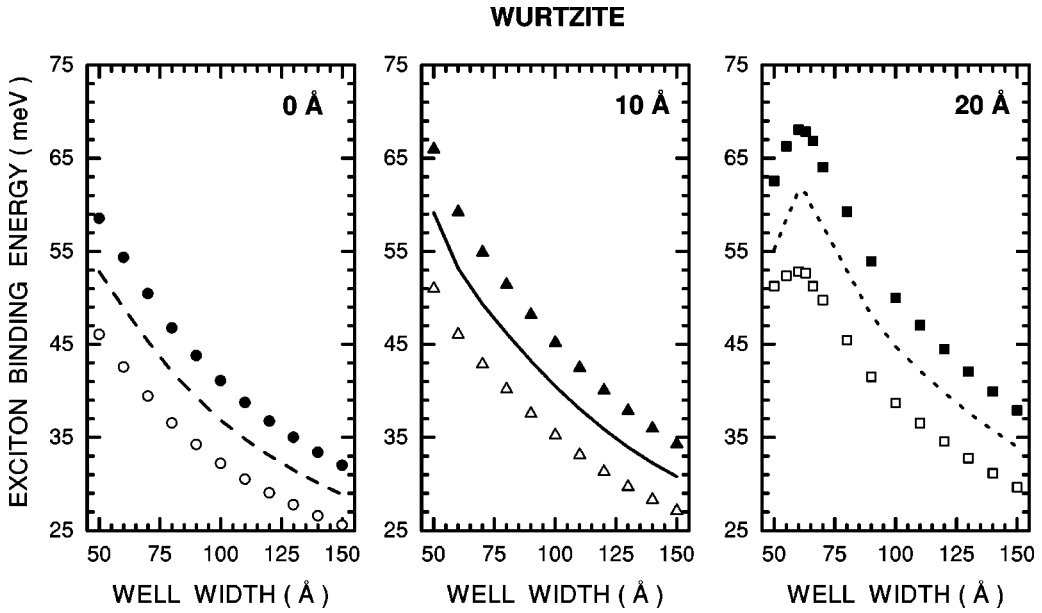

FIG. 2. The well width dependence of the ground state exciton binding energy $E_b(w_a,w)$ in wurtzite GaN/$Al_{0.3}Ga_{0.7}$N single QWs with abrupt interfaces (left panel), 10 Å (central panel), and 20 Å (right panel) wide interfaces. The results depicted with long dashed, solid, and dotted lines were obtained considering the gap energy and the carriers effective masses given in Table I. The black circles, triangles, and squares show the ground state exciton binding energy $E_b(w_a,w)$ calculated considering that the electron and heavy-hole masses are, respectively, +15 and +30 % heavier than those in Table I. The open circles, triangles, and squares show the ground state exciton binding energy $E_b(w_a,w)$ calculated considering that the electron and heavy-hole masses are, respectively, −15 and −30 % lighter than those in Table I.

finement in GaN/Al_xGa_{1-x}N single QWs are small (less than 5 and 10 meV when $w=10$ and $w=20$ Å, respectively, for 80 Å wide wells), the interface related corrections on the electron and heavy-hole energy are much bigger, and consequently the nonabrupt interface related ground state exciton energy blueshift is remarkable. This is shown in Fig. 3 and Fig. 4, that present the behavior of the ground state exciton energy in zinc-blende and wurtzite GaN/$Al_{0.3}Ga_{0.7}$N single QWs as a function of the abrupt well width w_a (lines and symbols in Figs. 3 and 4 have the same meaning as in Figs. 1 and 2). In these figures, the ground state exciton energy blueshift increases when the interface widths are thicker. The

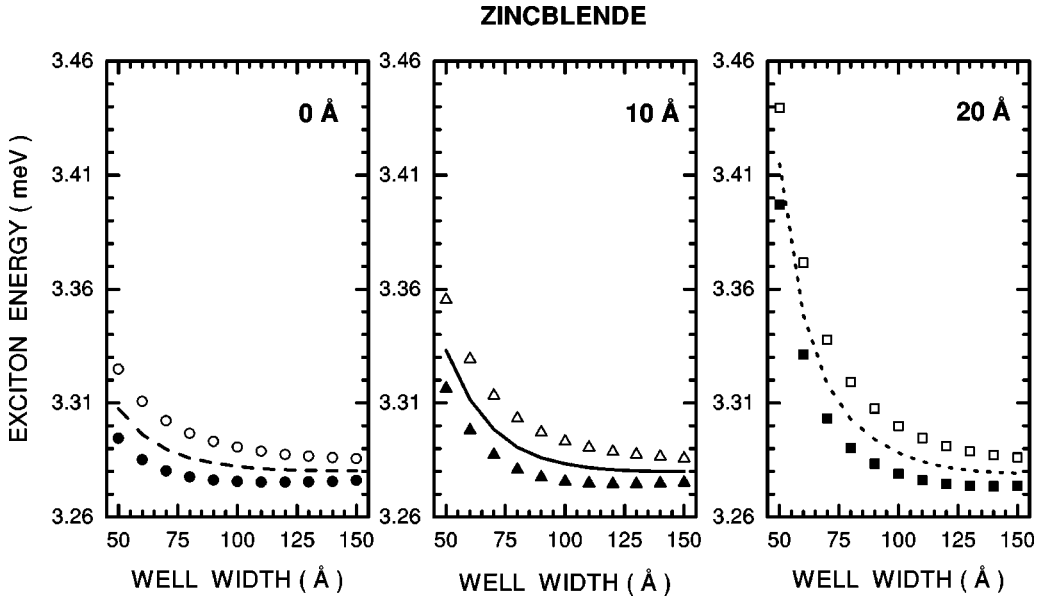

FIG. 3. The well width dependence of the ground state exciton energy $E_{ex}(w_a,w)$ in zinc-blende GaN/$Al_{0.3}Ga_{0.7}$N single QWs with abrupt interfaces (left panel), 10 Å (central panel), and 20 Å (right panel) wide interfaces. The results depicted with long dashed, solid, and dotted lines were obtained considering the gap energy and the carriers effective masses given in Table I. The black circles, triangles, and squares show the ground state exciton energy $E_{ex}(w_a,w)$ calculated considering that the electron and heavy-hole masses are, respectively, +15 and +30 % heavier than those in Table I. The open circles, triangles, and squares show the ground state exciton energy $E_{ex}(w_a,w)$ calculated considering that the electron and heavy-hole masses are, respectively, −15 and −30 % lighter than those in Table I.

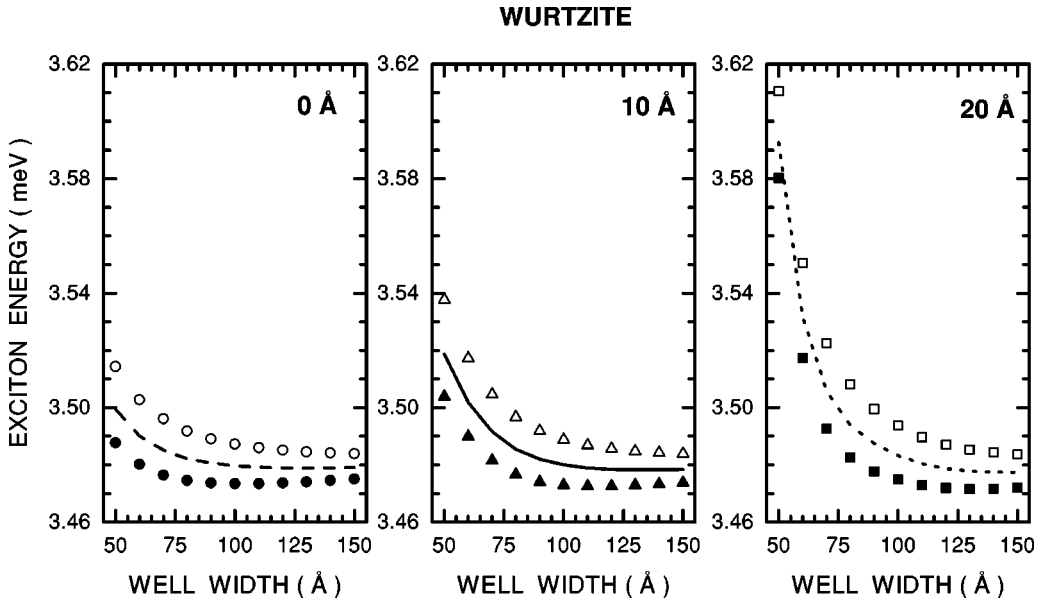

FIG. 4. The well width dependence of the ground state exciton energy $E_{ex}(w_a, w)$ in wurtzite $GaN/Al_{0.3}Ga_{0.7}N$ single QWs with abrupt interfaces (left panel), 10 Å (central panel), and 20 Å (right panel) wide interfaces. The results depicted with long dashed, solid, and dotted lines were obtained considering the gap energy and the carriers effective masses given in Table I. The black circles, triangles, and squares show the ground state exciton energy $E_{ex}(w_a, w)$ calculated considering that the electron and heavy-hole masses are, respectively, +15 and +30 % heavier than those in Table I. The open circles, triangles, and squares show the ground state exciton energy $E_{ex}(w_a, w)$ calculated considering that the electron and heavy-hole masses are, respectively, −15 and −30 % lighter than those in Table I.

strong interface related exciton energy blueshift is a consequence of the mean well width shortening due to the existence of nonabrupt interfaces in $GaN/Al_xGa_{1-x}N$ single QWs. Comparing Fig. 3 to Fig. 4, one can see that for a given well width, the ground state exciton energy in $GaN/Al_{0.3}Ga_{0.7}N$ zinc-blende QWs is always smaller than in similar wurtzite QWs, while nonabrupt interface effects are more important in the former than in the latter. This is basically a consequence of the fact that (i) the GaN gap energy of the former is smaller than that of the latter and (ii) the car-

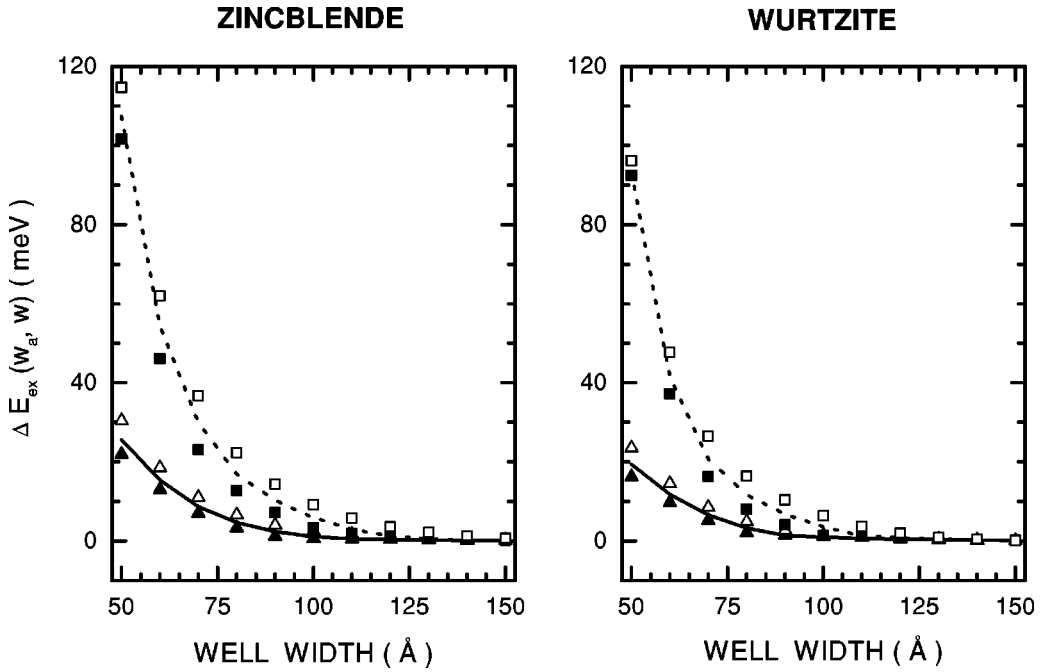

FIG. 5. The interface related ground state exciton energy blueshift $\Delta E_{ex}(w_a, w) = E_{ex}(w_a, w) - E_{ex}(w_a, w=0)$ in zinc-blende (left panel) and wurtzite (right panel) $GaN/Al_{0.3}Ga_{0.7}N$ single QWs. The results depicted by solid (dotted) lines were obtained considering $w = 10$ Å wide ($w = 20$ Å), and the electron and heavy-hole masses given in Table I. The results represented by open triangles and squares show $\Delta E_{ex}(w_a, w)$ calculated considering that the electron and heavy-hole masses are, respectively, −15 and −30 % lighter than those in Table I, while those represented by black triangles and squares show $\Delta E_{ex}(w_a, w)$ calculated considering that the electron and heavy-hole masses are, respectively, +15 and +30 % heavier than those in Table I.

riers QW depth confinement energy in the former (489 meV for electrons, 210 meV for heavy holes) is also bigger than in the latter (437 meV for electrons, 187 meV for heavy-holes).

The partial superposition of the regions delimited by black and open symbols in the panels of Figs. 3 and 4 is important. It means that the uncertainty on the carriers effective masses in zinc-blende and wurtzite $GaN/Al_xGa_{1-x}N$ single QWs can hide the existence of nonabrupt interfaces in actual samples. In fact, according to the variations on the carriers effective masses assumed in this work, the ground state exciton energy in 80 Å wide zinc-blende (wurtzite) $GaN/Al_{0.3}Ga_{0.7}N$ single QWs can be found between 3.297 eV (3.492 eV) and 3.290 eV (3.483 eV) whether the interfaces are sharp or as wide as 10 Å. Indeed, when the sharp interface picture is used to explain measurements of the ground state exciton energy in actual $GaN/Al_xGa_{1-x}N$ single QWs, an underestimate of the well width of the sample have to be considered to be achieved a better agreement between measurements and theoretical calculations. The results presented in this work allow us to suggest that the underestimation of the well width can be as high as 20 Å. Another direct consequence is that methods for evaluation of the carriers effective masses which need a comparison with the ground state confinement related exciton energy calculated within the abrupt interface picture are of limited precision.

Figure 5 presents a clear picture of the interface related exciton energy blueshift $\Delta E_{ex}(w_a,w)=E_{ex}(w_a,w)-E_{ex}(w_a,w=0)$ behavior in nonabrupt zinc-blende and wurtzite $GaN/Al_{0.3}Ga_{0.7}N$ QWs with interface widths $w=10$ Å (solid lines and triangles) and $w=20$ Å (dotted lines and squares). By comparing the left and right panels of Fig. 5, one can observe that for a given well width, the nonabrupt interface related confined exciton energy blueshift $\Delta E_{ex}(w_a,w)$ is always a little bigger in zinc-blende than in wurtzite QWs. In both phases, $\Delta E_{ex}(w_a,w)$ is stronger in the case of thin wells, but decreases when the wells are wider. It can be as big as ~ 100 meV (~ 25 meV) in the case of 50 Å wide wells with 20 Å (10 Å) interfaces (several times stronger than in similar $GaAs/Al_{0.3}Ga_{0.7}As$ QWs), and less than 3 meV for well widths larger than 100 Å. These figures highlight the strong interface related contribution to the exciton energy blueshift in $GaN/Al_xGa_{1-x}N$ wells due to the carriers confinement. Since the GaN zinc-blende lattice constant is $a=4.5$ Å and the wurtzite structure parameter in the growth direction $c=5.1$ Å, a 10 Å interface width has only about two monolayers, which is less than the thickness fluctuations suggested to exist in recent photoluminescense experiments performed by Smith *et al.*,[8] in $GaN/Al_xGa_{1-x}N$ multiple QWs, and the graded interface width in GaN/(AlGa)N single QWs obtained by Behr *et al.*[9] according to their resonant Raman scattering measurements. Consequently, it seems absolutely necessary to take into account the existence of nonabrupt interfaces when studying the quantum confined related exciton energy blueshift in $GaN/Al_xGa_{1-x}N$ wells.

All the previous presented and discussed results were obtained considering an aluminum molar fraction $x=0.3$ in the $Al_xGa_{1-x}N$ barriers. Considerable degree of tuning on the confinement related exciton based light emission can be obtained by changing x, e.g., the confinement well depth, suggesting that it is important to know how the confined exciton

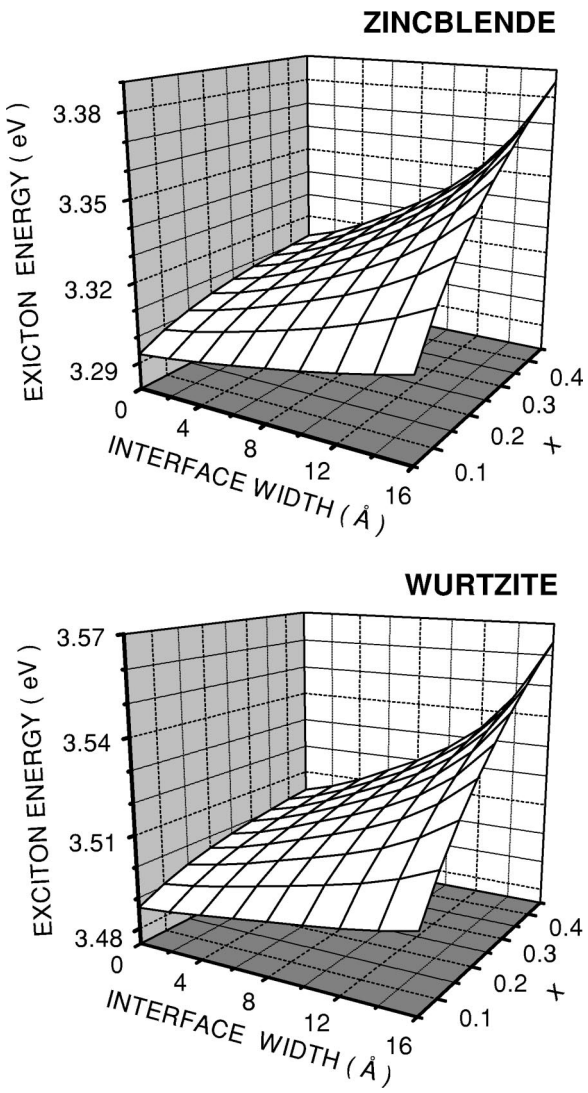

FIG. 6. The dependence of the ground state confine exciton energy $E_{ex}(w_a,w)$ in zinc-blende (top) and wurtzite (bottom) 50 Å wide $GaN/Al_xGa_{1-x}N$ single QWs on the interface width w and on the aluminum molar fraction x. The surfaces were calculated considering the gap energy and the carriers effective masses given in Table I.

energy changes with the variation of the aluminum molar fraction in nonabrupt $GaN/Al_xGa_{1-x}N$ wells. The dependence of the ground state exciton energy in 50 Å wide zinc-blende and wurtzite $GaN/Al_xGa_{1-x}N$ ($x<0.4$) single QWs on the nonabrupt interface width w and on the aluminum molar fraction x is presented in the top and the bottom of Fig. 6, respectively. This dependence is a little stronger in the zinc-blende phase than in the wurtzite phase. Finally, the interface effects on the exciton energy is shown to be more relevant when the aluminum molar fraction is higher, which is due to the enhancement of the confinement degree.

IV. CONCLUDING REMARKS

Instead of giving a detailed description of interface roughness in quantum wells, the nonabrupt interface description in this work should be recognized as a way to provide a mean estimate for the interface potential and carriers effective

masses resulting from fluctuations on the interface thickness in integral multiples of one monolayer. The well has to be wide enough ($w_a > 30$ Å) for the concept of mean fluctuation roughness to make sense. Consequently, the nonabrupt interface model presented in this work can not be very good to describe, for example, localization effects related with well thickness variation of few monolayers.

Recently, Smith *et al.*[8] have investigated optical transitions in very thin (~ 25 Å GaN layers) $GaN/Al_{0.07}Ga_{0.93}N$ multiple quantum wells. They observed an excitonic transition peak blueshift of 54 and 79 meV at 10 and 300 K, respectively, and have attributed the 25 meV difference between the blueshifts as due to the recombination of localized excitons (at 10 K) and free excitons (at 300 K). Arguing the enhancement of the exciton binding energy in multiple quantum wells also makes band-to-band recombination less likely, Smith *et al.*[8] have concluded that the 25 meV difference can be interpreted as a measure of the exciton localization energy, which suggests a well thickness fluctuation of ± 4 Å. Using the nonabrupt interface model presented in this work to describe interface effects in samples as thin as those of Smith *et al.*[8], if instead of an abrupt GaN abrupt well it is considered nonabrupt 25 ± 4 Å wide $GaN/Al_{0.07}Ga_{0.93}N$ QWs whose interfaces are 8 Å thick, the calculated blueshift can agree with the measurement. However, explaining the variation of the blueshift with the temperature as measured by Smith *et al.*[8] is beyond the conceptual framework of the nonabrupt interface model presented in this work.

In conclusion, the effects of nonabrupt interfaces on the ground state exciton energy in zinc-blende and wurtzite $GaN/Al_xGa_{1-x}N$ QWs were evaluated. It was obtained that the ground state exciton energy blueshift due to the existence of nonabrupt interfaces in $GaN/Al_xGa_{1-x}N$ zinc-blende single quantum wells is a little higher than those in similar wurtzite structures. The calculations showed that the interface related confined exciton blueshifts are stronger in thin quantum wells. The results allow us to suggest that to achieve a better understanding of the confined exciton based emission properties in actual $GaN/Al_xGa_{1-x}N$ QWs, it is necessary to use models in which the existence of nonabrupt interfaces is taken into account. Finally, although recent experimental results on the optical properties of $GaN/Al_xGa_{1-x}N$ QWs have been published,[2–10] they are very limited. It was not feasible to use them to test the nonabrupt interface model proposed in this work, specially because information related to the interface characterization were not given in those publications, as well as the photoluminescence peaks dependence on well widths in the range 50 to 150 Å. Nevertheless, the presented results are worthy of experimental confirmation within their limit of validity.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997); S. N. Mohammad and H. Morkoç, Prog. Quantum Electron. **20**, 361 (1996); I. Akasaki and H. Amano, Jpn. J. Appl. Phys. **36**, 5393 (1997), and references therein.

[2] M. A. Khan, R. A. Skogman, J. M. Van Hove, S. Krishnankutty, and R. M. Kolbas, Appl. Phys. Lett. **56**, 1257 (1990).

[3] G. Martin, S. Strite, A. Botchkarev, A. Agarwal, A. Rockett, H. Morkoç, W. R. L. Lambrecht, and B. Segall, Appl. Phys. Lett. **65**, 610 (1994).

[4] A. Salvador, G. Liu, W. Kim, Ö. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3322 (1995).

[5] M. F. MacMillan, L. L. Clemen, R. P. Devaty, W. J. Choyke, M. Asif Khan, J. N. Kuznia, and S. Krishnankutty, J. Appl. Phys. **80**, 2378 (1996).

[6] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, S.-H. Wei, M. Asif Khan, and C. J. Sun, Appl. Phys. Lett. **68**, 2784 (1996).

[7] R. Cingolani, G. Coli', R. Rinaldi, L. Calcagnile, H. Tang, A. Botchkarev, W. Kim, A. Salvador, and H. Morkoç, Phys. Rev. B **56**, 1491 (1997).

[8] M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, W. Kim, and H. Morkoç, Appl. Phys. Lett. **69**, 2453 (1996).

[9] D. Behr, R. Niebuhr, J. Wagner, K.-H. Bachem, and U. Kaufmann, Appl. Phys. Lett. **70**, 363 (1997).

[10] M. F. MacMillan, R. P. Devaty, W. J. Choyke, M. Asif Khan, and J. N. Kuznia, J. Appl. Phys. **80**, 2372 (1996).

[11] J. Holst, L. Eckey, A. Hoffmann, I. Broser, B. Schöttker, D. J. As, D. Schikora, and K. Lischka, Appl. Phys. Lett. **72**, 1439 (1998), and references therein.

[12] K. H. Ploog, O. Brandt, H. Yang, and T. Trampert, Thin Solid Films **306**, 231 (1997), and references therein.

[13] S. Strite and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).

[14] G. Ramírez-Flores, H. Navarro-Contreras, and A. Lastras-Martínez, Phys. Rev. B **50**, 8433 (1994).

[15] T. Lei, T. D. Moustakas, R. J. Graham, Y. He, and S. J. Berkowitz, J. Appl. Phys. **71**, 4933 (1992).

[16] M. Fanciulli, T. Lei, and T. D. Moustakas, Phys. Rev. B **48**, 15 144 (1993).

[17] M. Mizuta, S. Fujieda, Y. Matsumoto, and T. Kawamara, Jpn. J. Appl. Phys., Part 2 **25**, L945 (1986).

[18] M. J. Paisley, Z. Sitar, J. B. Posthill, and R. F. Davis, J. Vac. Sci. Technol. A **7**, 701 (1989).

[19] S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkoç, J. Vac. Sci. Technol. A **9**, 1924 (1991).

[20] T. Lei, M. Fanciulli, R. J. Molnar, T. D. Moustakas, R. J. Graham, and J. Scanlon, Appl. Phys. Lett. **95**, 944 (1991).

[21] W. R. L. Lambrecht and B. Segall, Phys. Rev. B **43**, 7070 (1991).

[22] M. E. Lin, G. Xue, G. L. Zhou, J. E. Greene, and H. Morkoç, Appl. Phys. Lett. **63**, 932 (1993).

[23] M. Drechsler, B. K. Meyer, D. M. Hoffmann, D. Detchprohm, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **34**, L1178 (1995).

[24] B. K. Meyer, D. Volm, A. Graber, H. C. Alt, T. Detchprohm, A. Amano, and I. Akasaki, Solid State Commun. **95**, 597 (1995).

[25] P. Perlin, E. Litwin-Staszewska, B. Suchanek, W. Knap, J. Camassel, T. Suski, R. Piotrzkowski, I. Grzegory, S. Porowski, E.

Kaminska, and J. C. Chervin, Appl. Phys. Lett. **68**, 1114 (1996), and references therein.
[26] J. S. Im, F. Steuber, V. Härle, F. Scholz, and A. Hangleiter, Appl. Phys. Lett. **70**, 631 (1997).
[27] Y.-N. Xu and W. Y. Ching, Phys. Rev. B **48**, 4335 (1993).
[28] K. Miwa and A. Fukumoto, Phys. Rev. B **48**, 7897 (1993).
[29] A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, Phys. Rev. B **48**, 11 810 (1993).
[30] E. A. Albanesi, W. R. L. Lambrecht, and B. Segall, Phys. Rev. B **48**, 17 841 (1993).
[31] A. F. Wright and J. S. Nelson, Phys. Rev. B **50**, 2159 (1994).
[32] M. Suzuki, T. Uenoyama, and A. Yanase, Phys. Rev. B **52**, 8132 (1995).
[33] T. Uenoyama and M. Suzuki, Appl. Phys. Lett. **67**, 2527 (1995).
[34] W. J. Fan, M. F. Li, T. C. Chong, and J. B. Xia, J. Appl. Phys. **79**, 188 (1996), and references therein; W. J. Fan, M. F. Li, T. C. Chong, and J. B. Xia, Solid State Commun. **97**, 381 (1996).
[35] K. Kim, W. R. L. Lambrecht, B. Segall, and M. van Schilfgaarde, Phys. Rev. B **56**, 7363 (1997), and references therein.
[36] Y. C. Yeo, T. C. Chong, and M. F. Li, J. Appl. Phys. **83**, 1429 (1998), and references therein.
[37] C. H. Kim and B.-H. Han, Solid State Commun. **106**, 127 (1998), and references therein.
[38] B. Jogai, Solid State Commun. **107**, 345 (1998), and references therein.
[39] M. A. Herman, D. Bimberg, and J. Christen, J. Appl. Phys. **70**, R1 (1991).
[40] J. R. Leite, G. A. Farias, and V. N. Freire (private communication).
[41] G. Mohs, T. Aoki, R. Shimano, M. Kuwata-Gonokami, and S. Nakamura, Solid State Commun. **108**, 105 (1998), and references therein.
[42] A. Satake, Y. Masumoto, T. Miyajima, T. Asatsunma, F. Nakamura, and M. Ikeda, Phys. Rev. B **57**, R2401 (1998).
[43] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **70**, 2822 (1997).
[44] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **70**, 981 (1997).
[45] T. Y. Chung and K. J. Chang, Semicond. Sci. Technol. **13**, 876 (1998).
[46] P. Bigenwald, P. Christol, A. Alemu, and B. Gil, J. Cryst. Growth **189**, 119 (1998).
[47] 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. Hiramatsu, and T. Detchprohm, Phys. Rev. B **53**, 16 543 (1996).
[48] 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).
[49] A. K. Viswanath, J. I. Lee, D. Kim, C. R. Lee, and J. Y. Leem, Phys. Rev. B **58**, 16 333 (1998).
[50] P. J. Price and F. Stern, Surf. Sci. **132**, 577 (1983).
[51] V. N. Freire, M. M. Auto, and G. A. Farias, Superlattices Microstruct. **1**, 17 (1992); R. Renan, V. N. Freire, M. M. Auto, and G. A. Farias, Phys. Rev. B **48**, 8446 (1993); M. C. A. Lima, G. A. Farias, and V. N. Freire, *ibid.* **52**, 5777 (1995); E. C. Ferreira, J. A. P. da Costa, G. A. Farias, and V. N. Freire, Superlattices Microstruct. **17**, 397 (1995).
[52] G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Éditions de Physique, Paris, 1992), and references therein.
[53] *Semiconductors, Physics of Group IV Elements and III-V Compounds*, edited by K. H. Hellwage and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer, Berlin, 1982).
[54] W. J. Fan, M. F. Li, T. C. Chomg, and J. B. Xia, Superlattices Microstruct. **4**, 251 (1996).
[55] A. F. Wright and J. S. Nelson, Appl. Phys. Lett. **66**, 3051 (1995).
[56] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).
[57] H. Angerer, D. Brunner, F. Freudenberg, O. Ambacher, M. Stutzmann, R. Höpler, T. Metzger, E. Born, G. Dollinger, A. Bergmaier, S. Karsch, and H.-J. Körner, Appl. Phys. Lett. **71**, 1504 (1997).
[58] D. K. Wickenden, C. B. Bargeron, W. A. Bryden, J. Miragliptta, and T. J. Kistenmacher, Appl. Phys. Lett. **65**, 2024 (1994).
[59] M. R. Khan, Y. Koide, H. Itoh, N. Sawaki, and I. Akasaki, Solid State Commun. **60**, 509 (1986).
[60] Y. Koide, H. Itoh, M. R. Khan, K. Hiramatu, N. Sawaki, and I. Akasaki, J. Appl. Phys. **61**, 4540 (1987).
[61] M. Smith, G. D. Chen, J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, W. Kim, Ö. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3387 (1995).
[62] Y. C. Yeo, T. C. Chong, and M. F. Li, J. Appl. Phys. **83**, 1429 (1998), and references therein.
[63] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett. **15**, 327 (1969).
[64] B. Monemar, Phys. Rev. B **10**, 676 (1974).
[65] P. B. Perry and R. F. Rutz, Appl. Phys. Lett. **33**, 319 (1978).
[66] Y. Ando and T. Itoh, J. Appl. Phys. **61**, 1497 (1987).
[67] The nonabrupt interface thickness should present a small increase when the actual $GaN/Al_xGa_{1-x}N$ single QWs becomes wider, which can be due to lattice stress relaxation, diffusion processes enhancement, and/or control problems on the monolayers growth process. Since no experimental data seems to have been published concerning this hypothesis to the knowledge of the authors, it is not considered in this work.
[68] Using the formula $E_{b(3D)} = 13.6\mu_{e\text{-}h}/\epsilon^2$ (in eV) and the values for the electron and heavy-hole effective masses given in Table I, the 3D GaN exciton binding energy in the zinc-blende and wurtzite phases is 26 meV.