Compositional disorder in $GaAs_{1-x}N_x$:H investigated by photoluminescence

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Compositional disorder is investigated by means of photoluminescence (PL) and PL excitation (PLE) measurements in as-grown and hydrogen-irradiated $GaAs_{1-x}N_x$ samples ($x \leqslant 0.21\%$). The dependence of the linewidth of the PLE free-exciton band on N concentration agrees well with that predicted by a theoretical model developed for a purely random alloy. We also find that hydrogen irradiation and ensuing nitrogen passivation reduce significantly the broadening of the free-exciton band. This result is consistent with a removal by hydrogen of the static disorder caused by nitrogen. Finally, an analysis of the dependence of the Stokes shift on the free-exciton linewidth shows that free carriers are thermalized even at low temperature, another indication of a low degree of disorder in the investigated samples.

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I. INTRODUCTION

The striking effects of nitrogen incorporation on the electronic properties of $GaAs_{1-x}N_x$ have been studied in great detail in the recent years.[1] In particular, the giant bowing of the energy gap with increasing N concentration has been the object of many reports, both theoretical[2,3] and experimental.[4,5] Other peculiar effects include an uncommonly large and abrupt increase in the electron effective mass upon nitrogen incorporation, which is accompanied by a reduction in the extent of the excitonic wave function.[6] All these experimental facts are explained in terms of an interaction between the host crystal states and localized levels associated with nitrogen complexes leading to strong nonlinear modifications of the material's band structure.[2,3]

The response to irradiation with atomic hydrogen is another peculiarity of the $GaAs_{1-x}N_x$ alloy. It is found, indeed, that all the electronic and structural properties induced by N insertion into the GaAs lattice can be finely controlled by H implantation.[7–10] As a matter of fact, hydrogen irradiation "transforms" a $GaAs_{1-x}N_x$ sample with a given concentration x into a sample with virtually any desired concentration in the range between 0% and x.[7–9] This intriguing behavior is explained by the formation of N-H complexes that neutralize the perturbation exerted by N atoms on the host matrix.[11,12] Although a fine tuning of the energy gap and of the electron effective mass by post-growth hydrogenation might have a wide range of applications, further studies are required before fabricating devices or nanostructures based on hydrogenated $GaAs_{1-x}N_x$ (Ref.13). To this respect, an analysis of the compositional and structural disorder of $GaAs_{1-x}N_x$ samples, and how such disorder varies upon H irradiation is an issue of special interest. In particular, the extent and N concentration dependence of the energy broadening of radiative recombinations can provide valuable information regarding the distribution of nitrogen atoms in $GaAs_{1-x}N_x$ alloys.

In this paper, we report on the effects of compositional disorder on the optical properties of $GaAs_{1-x}N_x$ samples ($0.043\% \leqslant x \leqslant 0.21\%$), both as-grown and post-growth irradiated with atomic hydrogen. The broadening of the free-exciton (FE) linewidth as measured by photoluminescence excitation (PLE) is compared with the predictions of a statistical model introduced to describe the effects of *random* compositional disorder on the excitonic density of states (DOS) of semiconductor alloys,[14–16] and recently extended to $GaAs_{1-x}N_x$.[17–19] for both as-grown and hydrogenated samples a quite good agreement is found here with the predictions of the model reported in Ref. 17 In particular, after hydrogenation the FE linewidth depends only on the concentration of unpassivated nitrogen, x_{eff}, regardless of the initial sample composition. This result agrees with a substantial removal by hydrogen of the static disorder caused by nitrogen, as recently established by an x-ray absorption fine structure study in $GaAs_{1-x}N_x$ before and after hydrogenation.[20] In other words, the H-driven tuning of N-induced properties is obtained at almost no expense of the $GaAs_{1-x}N_x$ quality, that is an important outcome of our investigation. Finally, the relationship between the Stokes shift—namely, the energy difference between the FE peak energies measured by PLE and PL—and the FE linewidth is compared with a model describing carrier relaxation in the presence of alloy disorder. Such comparison shows that free-excitons are thermalized even at low temperature, thus confirming the low degree of disorder in these ternary alloys at low x.

II. EXPERIMENTAL DETAILS

We studied three $GaAs_{1-x}N_x$/GaAs epitaxial layers (having $x=0.043\%$, 0.095%, and 0.21%, and thickness 0.5 μm) grown by metalorganic vapor phase epitaxy.[19] The N concentration was determined by high-resolution x-ray diffraction measurements. The samples were irradiated at 300 °C by a low-energy ion gun (beam energy ~100 eV) with different hydrogen doses ($d_H = 1.0\times10^{18}$–5.6×10^{18} ions/cm^2). PL and PLE measurements were performed using the 532 nm line of a vanadate-Nd laser and a Ti-sapphire tunable laser as the excitation sources. The luminescence signal was dispersed by a double 0.75 m monochromator and detected by a

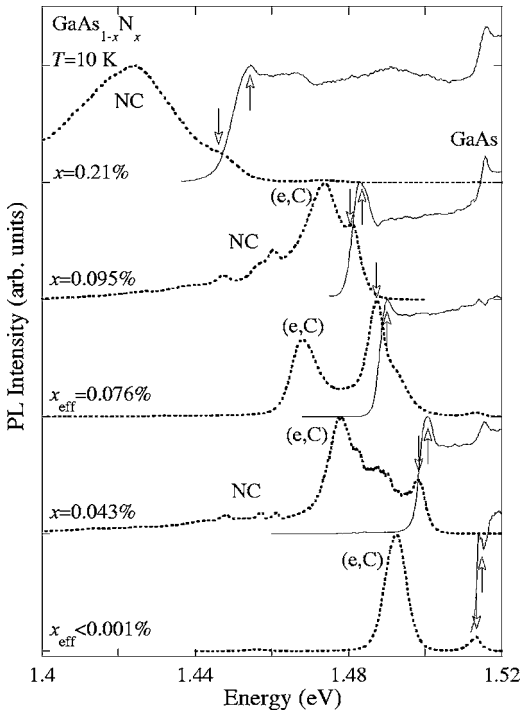

FIG. 1. Peak-normalized photoluminescence (PL, dotted line) and PL excitation (PLE, solid line) spectra at $T=10$ K of a selection of the $GaAs_{1-x}N_x$ samples studied in this work. Nitrogen concentrations are given. For the hydrogenated samples, the effective N concentration x_{eff} is also specified. Upward and downward arrows mark the free-exciton energy for PLE and PL spectra, respectively. (e,C) indicates the free-electron to neutral-carbon recombination, and NC indicates carrier recombination from nitrogen complexes. From topmost to bottommost PLE spectrum the detection energies are $E_{det}=1.423$ eV ($x=0.21\%$), 1.472 eV ($x=0.095\%$), 1.466 eV ($x_{eff}=0.076\%$), 1.448 eV ($x=0.043\%$), and 1.511 eV ($x_{eff}<0.001\%$).

GaAs photomultiplier operating in a single-photon counting mode.

III. RESULTS AND DISCUSSION

A. Linewidth analysis

PL and PLE spectra of the as-grown samples as well as of two hydrogenated samples are shown in Fig. 1. As reported elsewhere,[6,8] the PL spectra present several features that are labeled in the figure. Downward pointing arrows indicate the $GaAs_{1-x}N_x$ free-exciton emission, (e,C) labels a band due to recombination of a free-electron with a hole bound to an acceptor, most likely carbon, and NC refers to recombination bands from different nitrogen clusters. As x increases the levels related to NC are progressively taken in by the states of the continuum moving at lower energy.[2] One can notice that the peak energy of the (e,C) transition displays a nonmonotonic dependence between $x=0.043\%$ and $x=0.095\%$. This can be attributed to the variation of tensile strain induced by the presence (or passivation, in hydrogenated samples) of nitrogen atoms.[10,21] Indeed, for increasing N concentration the top of the valence band acquires a more pronounced light-hole character and, in turn, the binding energy of the acceptor impurity decreases due to the decrease of the hole mass. In the PLE spectra, upward arrows mark the $GaAs_{1-x}N_x$ FE peaks. Moreover, the GaAs FE exciton peak at 1.515 eV is observed together with features at lower energy likely due to N cluster states resonant with the continuum of the above-gap states of $GaAs_{1-x}N_x$. The spectra of the hydrogenated samples illustrate the fine tuning of the effective N concentration by means of H irradiation. Indeed, irradiation of the $x=0.095\%$ sample with $d_H=3.5\times10^{18}$ ions/cm^2 produces a sample with $x_{eff}=0.076\%$ (as estimated from the energy position of the free-exciton peak in PLE, E_{FE}), while a dose $d_H=5.6\times10^{18}$ ions/cm^2 leads to an almost complete passivation ($x_{eff}<0.001\%$) of the $x=0.043\%$ sample. At the same time, the spectral features associated with N clusters disappear upon hydrogenation because of the formation of N-H complexes.[22,23]

We now estimate the degree of randomness of the N distribution in $GaAs_{1-x}N_x$, as well as the effect of hydrogen on it, by comparing the broadening of the exciton energy distribution predicted by the model of Ref. 17 with the experimental FE linewidth. This latter is derived from low-temperature PLE spectra as exemplified in Fig. 2 for a sample with $x=0.095\%$ both untreated and irradiated with different H doses. The corresponding PL spectra taken at the same temperature and power density are also shown in the figure. First, we find that both a light- (lh) and a heavy-hole (hh) component at low and high energy, respectively, contribute to the FE band in the PLE spectrum. The lattice mismatch between the $GaAs_{1-x}N_x$ epitaxial layer and the GaAs substrate produces, indeed, a tensile strain[10,21] that removes the degeneracy between light- and heavy-holes typically found at the valence band maximum of zinc blende semiconductors. A detailed study of the evolution of this splitting with increasing N concentration and H dose performed by means of polarization-dependent PLE measurements will be reported elsewhere.[24] Second, we notice that the FE band is redshifted in PL with respect to its energy in PLE by an amount labeled SS (Stokes shift). This energy difference is due to the fact that PL spectra are dominated by the recombination of thermalized photoexcited carriers. Carrier relaxation and thermalization mechanisms may depend on phonon-assisted hopping,[25] tunneling from one impurity center to another,[26,27] and a large variety of other phenomena that make less straightforward the establishment of a direct relationship between the FE linewidth as measured by PL and theoretical estimates of the disorder-induced broadening of the exciton DOS.[28] On the contrary, the PLE signal measured at a given detection energy, E_{det}, is proportional to the absorption coefficient α at the excitation photon energy, E_{ex}, and to the probability that photogenerated carriers relax to—and emit from—the states with energy E_{det}. Therefore, for a suitable choice of E_{det}, the PLE signal is a good approximation of α and, in turn, of the excitonic DOS. Nevertheless, the relative intensity between light- and heavy-hole excitons does not always reproduce the higher DOS expected for hh with respect to lh excitons, as shown in Fig. 2(a). We found (not shown here) that the intensity ratio between the light- and heavy-hole exciton peaks in the PLE spectrum may vary with E_{det}. Although a systematic study of this finding has

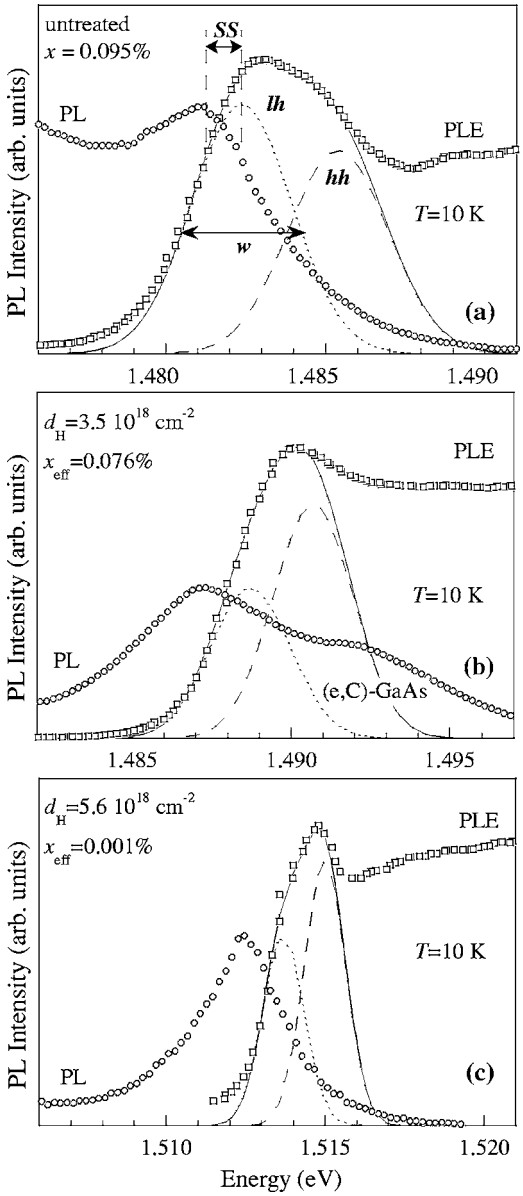

FIG. 2. Comparison between the photoluminescence (PL, circles) and PL excitation (PLE, squares) spectra at $T=10$ K of: (a) an untreated $x=0.095\%$ sample (PLE detection energy $E_{\mathrm{det}}=1.472$ eV); (b) a hydrogenated $x=0.095\%$ sample resulting in an effective N concentration $x_{\mathrm{eff}}=0.076\%$ ($E_{\mathrm{det}}=1.466$ eV) [(e,C)-GaAs in the PL spectrum indicates the free-electron to neutral-carbon recombination in the GaAs buffer layer]; (c) a hydrogenated $x=0.095\%$ sample resulting in an effective N concentration $x_{\mathrm{eff}}=0.001\%$ ($E_{\mathrm{det}}=1.510$ eV). The result of a fit of the free-exciton (FE) PLE band using two Gaussians is also shown (solid line), along with the FE light-hole (lh, dotted line) and heavy-hole (hh, dashed line) components.

been not performed yet, we carefully checked that the FE linewidth is independent of E_{det} for all samples considered. Finally, Fig. 2 shows that the FE linewidth reduces sizably with increasing hydrogen dose (from $w=3.7$ meV for $d_{\mathrm{H}}=0$ to $w=1.5$ meV for $d_{\mathrm{H}}=5.6\times10^{18}$ cm^{-2}). This is a quite interesting effect, since hydrogen acts in all respects as if it restored the compositional order lost upon N incorporation.

We now compare the experimental linewidth w of the light-hole component of the PLE excitonic band (extracted from the experimental data with a fit by two Gaussians[29] such as those shown in Fig. 2) with its theoretical estimate obtained following Ref. 17. All PLE spectra used for this analysis were recorded at a same temperature ($T=10$ K). In a generic random alloy $AB_{1-x}C_x$, the free-exciton band has a Gaussian line shape with a full width at half maximum w, whose dependence on x is given by[17]

$$w = \gamma\left(2\frac{\mathrm{d}E_{FE}}{\mathrm{d}x}\sqrt{\frac{2\ln 2(1-x)xV_c}{(4\pi/3)a_{\mathrm{ex}}^3}}\right). \tag{1}$$

According to this model, in a random alloy with low structural disorder, namely, with no sizable phase separation or clustering effects, the broadening of the excitonic band is entirely due to the potential fluctuations experienced by the free-exciton in regions of the sample where x and the energy gap change with respect to the nominal value. The exciton Bohr radius a_{ex} is the characteristic length over which the composition fluctuations are sampled and V_{c} is the volume of the primitive cell, namely $V_{\mathrm{c}}=a^3/4$ in zinc blende materials, where a is the lattice constant. For simplicity, a is kept fixed to its GaAs value (5.653 Å[30]) throughout our analysis. In practice, this volume can be regarded as the smallest region of the lattice over which an alloy fluctuation can occur. Finally, because of a certain degree of arbitrariness in the definition of V_{c} and of the effective exciton volume sampling lattice disorder,[15,16] γ has been introduced as a free fitting parameter in Eq. (1).

In order to estimate the FE broadening from Eq. (1), we need to know the exciton Bohr radius a_{ex}, and the rate of change of the FE peak energy, $\mathrm{d}E_{\mathrm{FE}}/\mathrm{d}x$, with N concentration. In Ref. 17 it was highlighted the importance of the choice of the electron effective mass values in order to get an estimate of a_{ex} in Eq. (1) through a hydrogenoid model ($a_{\mathrm{ex}}=\varepsilon_0\hbar^2/\mu e^2$, where $\mu^{-1}=m_e^{-1}+m_h^{-1}$ is the exciton effective mass, being m_{e} and m_{h} the electron and hole effective mass, respectively). Here, we overcome this problem by using a_{ex} values derived experimentally. In fact, we obtain the expectation value of the electron-hole in-plane distance squared, $\langle x_{eh}^2+y_{eh}^2\rangle=\langle r_{eh}^2\rangle$, and hence the exciton Bohr radius $a_{\mathrm{ex}}=\sqrt{\langle r_{eh}^2\rangle}/\sqrt{2}$ directly from the diamagnetic shift of the free-exciton energy.[6,8] This peak corresponds to the low-energy component of the FE resonance in PLE because of the relaxation processes favoring lower energy states. The a_{ex} values are listed in Table I (the uncertainty on these values results in an uncertainty in the calculated values of w equal to about 2%) along with the nominal and effective N concentration of the studied samples and the hydrogen dose to which the samples were exposed. The electron effective mass values corresponding to these a_{ex}'s imply a compositional dependence of m_{e} different from those discussed in Ref. 17. In fact, our electron mass data show a sudden change occurring for $x\sim0.1\%$,[6,8,31] a feature not reported by the works mentioned in Ref. 17, and accounted for, instead, by the model of Refs. 3 and 31. As for $\mathrm{d}E_{\mathrm{FE}}/\mathrm{d}x$, the dependence of E_{FE} on nitrogen concentration can be described by a power-law

TABLE I. Values of the exciton Bohr radius, a_{ex}, for all the samples studied in this paper, as obtained in Refs. 6 and 8 after division by $\sqrt{2}$ to take into account the different definition between the exciton Bohr radius and the in-plane extent of the exciton wave function. The uncertainty on a_{ex} is reported in parentheses. The nominal (x) and effective (x_{eff}) N concentrations are also given for each sample, along with the hydrogen dose (d_H) to which the sample was exposed.

x (%)	d_H (10^{18} ions/cm^2)	x_{eff} (%)	a_{ex} (nm)
0.043	0	0.043	8.70 (0.08)
0.043	2.0	0.039	8.73 (0.11)
0.043	5.6	<0.001	8.34 (0.07)
0.095	0	0.095	7.50 (0.08)
0.095	1.0	0.093	8.72 (0.09)
0.095	3.5	0.076	8.24 (0.16)
0.095	5.6	0.001	9.55 (0.10)
0.21	0	0.21	7.13 (0.10)

$$E_{FE}(x) = E_{FE}^0 + Ax^\beta, \tag{2}$$

where E_{FE}^0 is the energy of the FE in GaAs. By fitting Eq. (2) to the values of E_{FE} obtained from the PLE spectra, we obtain in eV units $E_{FE}(x)=E_{FE}^0-16.2\times x^{0.9}$, in good agreement with the theoretical predictions of a value of β ranging between 0.66 and 0.89.[2,32]

The full width at half maximum values of the FE band evaluated by Eq. (1) are compared in Fig. 3 with the experimental values of w. The agreement between experiment (full symbols) and theory (open squares) is quite good, both for the as-grown (full circles) and the hydrogenated (full triangles) samples.[33] In the case of fully-hydrogenated samples ($x_{eff}\leqslant 0.001\%$), the deviation from the theoretical predictions is most likely due to other disorder sources, which are not taken into account in Eq. (1). Their contribution amounts to about 1 meV as estimated from the PLE linewidth of the FE in the GaAs buffer layer of the same samples.[34] In Ref. 18, a configuration-related source of broadening due to anisotropic N-N interactions was invoked to give rise to additional broadening for $x\sim 0.2\%$. However, this feature is not observed by us and we can then conclude that such mechanism does not affect sizably our samples. The value of γ that best fits the experimental data shown in Fig. 3 is 0.38, very close to the value of 0.41 estimated in Ref. 15 by a quantum statistical approach. Finally, the small, abrupt "jump" occurring in the FE linewidth at about $x=0.1\%$ is the signature of a shrinking of a_{ex}, see Table I. This feature was well established in previous papers and is due to a sudden change in the electron effective mass value.[6,8,31] The agreement we found between the experimental observations and the predictions of Eq. (1) provides strong evidence that nitrogen atoms are randomly distributed in $GaAs_{1-x}N_x$ for $x\leqslant 0.21\%$, a precondition for the applicability of the model of Ref. 17, and that the hydrogenation process does not affect severely the randomicity of the N atom distribution. Therefore, H implantation does not introduce structural defects in the host lattice to such an extent as to largely affect the FE linewidth. Most interestingly, hydrogenation *decreases* the FE linewidth, as shown in Fig. 2 and reported in Table II, a sign of a sizably diminished disorder in the sample. This result is fully consistent with previous experimental findings and theoretical calculations in $GaAs_{1-x}N_x$ alloys. Indeed, x-ray absorption fine structure measurements in $GaAs_{1-x}N_x$ epitaxial layers showed that the Debye-Waller factor (which measures the static disorder induced by N incorporation in $GaAs_{1-x}N_x$) of the Ga-As bond length gradually *increases* with increasing N concentration, and it *decreases* back to the value characteristic of GaAs in fully N passivated samples.[20] On the theoretical side, first-principle calculations showed that hydrogenation of $GaAs_{1-x}N_x$ causes the conduction band to essentially recover the delocalized character and curvature it has in a N-free GaAs lattice, in agreement with the experimentally determined recovery of the GaAs electron effective mass upon hydrogenation.[8,31,35]

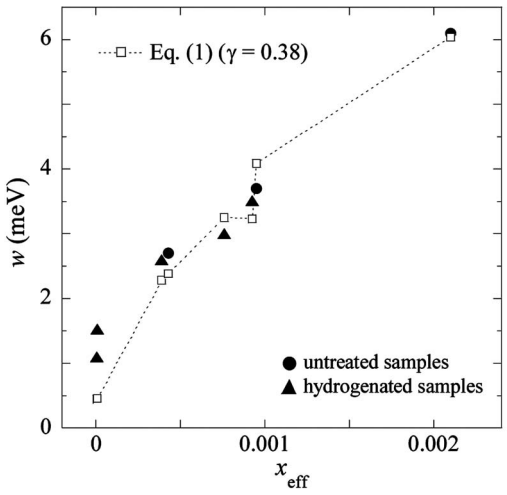

FIG. 3. Dependence of the experimental free-exciton linewidth w (full symbols) on the effective nitrogen concentration x_{eff}. Full circles refer to as-grown samples and full triangles refer to the hydrogenated samples. The theoretical predictions of Eq. (1) are also shown in the figure (open squares; the dashed line is a guide to the eye). Notice that the lowest x value used in the theoretical model is $x=0.001\%$.

B. Stokes shift analysis

In semiconductor alloys, the interplay between compositional disorder and carrier thermalization strongly influences the establishment of equilibrium conditions for free-excitons.[36–39] These processes are investigated here by an analysis of the dependence of the Stokes Shift on the degree of compositional disorder, as measured by the FE linewidth. We already pointed out that the Stokes shift shown in Fig. 2 is due to the fact that free carriers relax towards states of lower energy before they annihilate radiatively. Among the number of physical phenomena involved in the relaxation process, two main regimes were previously identified. In highly disordered systems, excitons relax toward and are trapped by local energy minima due to impurities or lattice

TABLE II. Values of the experimental FE linewidth, w, of the Stokes shift, SS, and of the effective carrier temperature, T_c, for all the samples studied in this work. The uncertainty associated with the experimental data is reported in parentheses. The nominal (x) and effective (x_{eff}) N concentrations are also given for each sample, along with the hydrogen dose (d_H) to which the sample was exposed. Note that the different T_c values are due to the different laser powers used for the different samples (T was kept at 10 K).

x (%)	d_H (10^{18} ions/cm^2)	x_{eff} (%)	w (meV)	SS (meV)	T_c (K)
0.043	0	0.043	2.7 (0.3)	1.6 (0.2)	14.3 (0.5)
0.043	2.0	0.039	2.6 (0.5)	0.6 (0.2)	16.0 (0.7)
0.043	5.6	<0.001	1.1 (0.1)	0.5 (0.2)	12.3 (1.2)
0.095	0	0.095	3.7 (0.4)	1.1 (0.3)	25.5 (0.8)
0.095	1.0	0.093	3.5 (0.5)	1.7 (0.2)	13.8 (0.7)
0.095	3.5	0.076	3.0 (0.6)	1.3 (0.2)	14.3 (1.0)
0.095	5.6	0.001	1.5 (0.2)	1.0 (0.2)	12.3 (0.9)
0.21	0	0.21	6.1 (0.6)	2.7 (0.5)	27.9 (0.9)

defects.[36,37] In this case, a linear relationship between SS and the FE linewidth is found.[36] When the disorder-induced broadening of the excitonic DOS is comparable with the carrier thermal energy, instead, a thermal quasiequilibrium is reached within the exciton population after exciton relaxation.[38,39] At low temperature (T=10 K) and for laser moderate power densities (few W/cm^2), the thermal energy is small (k_BT=0.86 meV). Therefore, a quasiequilibrium condition can be reached only in systems with a low degree of disorder. In this case, the PL intensity of the FE band is roughly proportional to the excitonic DOS, namely, to the absorption coefficient $\alpha(E)$, properly weighted with a Boltzmann distribution function[39,40]

$$I_{PL}(E) \propto \alpha(E)e^{-E/k_BT_c}. \quad (3)$$

In quasiequilibrium conditions, the effective carrier temperature, T_c, greater than or equal to that of the lattice, can be determined by an exponential fit of the ratio between the PL spectrum and the absorption coefficient of the free-exciton.[40] This fit is shown for the x=0.043% sample in Fig. 4, where the ratio between the PL intensity, $I_{PL}(E)$, and the PLE intensity, $I_{PLE}(E)$, displays an exponential dependence on energy with a T_c value (14.3 K) consistent with the nominal lattice temperature (T=10 K). This same procedure was used to determine the value of T_c in all samples, both as-grown and hydrogenated, thus showing that the exciton population in all our samples reached thermal equilibrium conditions.

This result is further supported by the functional dependence of the Stokes shift on the FE linewidth. In fact, an analysis of Eq. (3) shows the existence of a simple relationship between SS, w, and T_c whenever the broadening of the excitonic band can be described by a Gaussian function,[39] and quasithermalization rules the exciton distribution. In this case

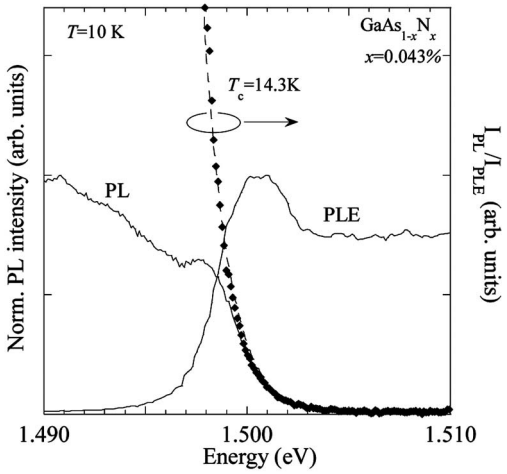

FIG. 4. Ratio between the photoluminescence (PL) and PL excitation (PLE) spectra of the sample with x=0.043% taken at 10 K and with excitation power density P_{ex}=3 W/cm^2 (full diamonds, right axis). The dashed line is the result of a fit performed with the Boltzmann distribution function (T_c=14.3 K), see Eq. (3). The PL and PLE spectra used in this procedure are also shown (solid lines, left axis). PLE detection energy E_{det}=1.448 eV.

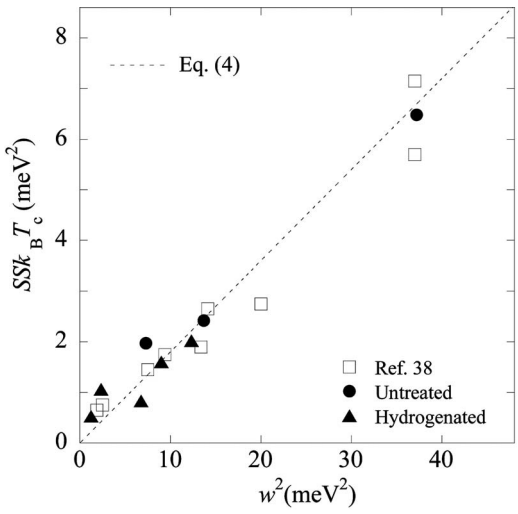

FIG. 5. Dependence of the product of the Stokes shift SS and the carrier thermal energy k_BT_c on the experimental linewidth squared w^2. w values as derived from PLE, see text, are reported in Table II. Full circles (triangles) refer to as-grown (hydrogenated) samples. The dashed line gives the behavior described by Eq. (4). Data from Ref. 38 (empty squares) are also shown for comparison.

$$\mathrm{SS}\ k_B T_c = 0.18 w^2. \quad (4)$$

In Fig. 5 the product $\mathrm{SS} k_B T_c$ is plotted as a function of w^2 for all samples (full symbols) together with the behavior predicted by Eq. (4) (dashed line). The experimental linewidths used are those shown in Fig. 3. The values of the Stokes shift were obtained by PL and PLE spectra taken at constant temperature ($T=10$ K), while T_c was determined as discussed above. The values of w, SS, and T_c used in Fig. 5 are listed in Table II, along with their experimental uncertainties. The quite good agreement between theory and experiment confirms the fundamental role played by thermalization in our samples. Data taken from Ref. 38 and relative to $In_xGa_{1-x}As/GaAs$ quantum wells are also shown in Fig. 5 as an example of a random, virtual crystal approximationlike alloy, which behaves according to the thermalization model.

IV. CONCLUSIONS

In summary, we have shown that a fully statistical model for random alloys well describes the dependence of the FE linewidth on nitrogen concentration in $GaAs_{1-x}N_x$, both as-grown and irradiated with hydrogen. Therefore, as-grown $GaAs_{1-x}N_x$ can be treated as a random alloy with a very low structural disorder, at least in the range of N concentration less than or equal to 0.21%. In agreement with previous structural measurements,[20] crystalline order is largely recovered upon irradiation with atomic hydrogen as demonstrated by the sizable decrease in the FE band linewidth of hydrogenated samples. Finally, the low degree of disorder in our samples is confirmed by unambiguous evidence that the free-exciton distribution after relaxation is ruled primarily by thermalization.

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[1] For a review see *Dilute Nitride Semiconductors: Physics and Technology*, edited by M. Henini (Elsevier, Oxford, UK, 2004).
[2] P. R. C. Kent and Alex Zunger, Phys. Rev. B **64**, 115208 (2001).
[3] A. Lindsay and E. P. O'Reilly, Phys. Rev. Lett. **93**, 196402 (2004).
[4] M. Weyers and M. Sato, Appl. Phys. Lett. **62**, 1396 (1993).
[5] T. Taliercio, R. Intartaglia, B. Gil, P. Lefebvre, T. Bretagnon, U. Tisch, E. Finkman, J. Salzman, M.-A. Pinault, M. Laügt, and E. Tournié, Phys. Rev. B **69**, 073303 (2004).
[6] F. Masia, A. Polimeni, G. Baldassarri Höger von Högersthal, M. Bissiri, M. Capizzi, P. J. Klar, and W. Stolz, Appl. Phys. Lett. **82**, 4474 (2003).
[7] A. Polimeni, G. Baldassarri H. v. H., M. Bissiri, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 201304(R) (2001).
[8] A. Polimeni, G. Baldassarri Höger von Högersthal, F. Masia, A. Frova, M. Capizzi, Simone Sanna, Vincenzo Fiorentini, P. J. Klar, and W. Stolz, Phys. Rev. B **69**, 041201(R) (2004).
[9] A. Polimeni and M. Capizzi, *Role of Hydrogen in Dilute Nitrides*, in *Physics and Applications of Dilute Nitrides*, edited by I. A. Buyanova and W. M. Chen (Taylor & Francis Books, Inc., New York, 2004).
[10] A. Polimeni, G. Ciatto, L. Ortega, F. Jiang, F. Boscherini, F. Filippone, A. Amore Bonapasta, M. Stavola, and M. Capizzi, Phys. Rev. B **68**, 085204 (2003).
[11] G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni, and M. Capizzi, Phys. Rev. B **71**, 201301 (2005).
[12] Mao-Hua Du, S. Limpijumnong, and S. B. Zhang, Phys. Rev. B **72**, 073202 (2005); W. B. Fowler, Kevin R. Martin, Kathryn Washer, and Michael Stavola, Phys. Rev. B **72**, 035208 (2005).
[13] M. Felici, A. Polimeni, G. Salviati, L. Lazzarini, N. Armani, F. Masia, M Capizzi, F. Martelli, M. Lazzarino, G. Bais, M. Piccin, S. Rubini, and A. Franciosi, Adv. Mater. **18**, 1993 (2006).
[14] J. Singh and K. K. Bajaj, Appl. Phys. Lett. **44**, 1075 (1984).
[15] M. Lee and K. K. Bajaj, J. Appl. Phys. **73**, 1789 (1993).
[16] G. Coli, K. K. Bajaj, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **78**, 7505 (2003).
[17] R. T. Senger and K. K. Bajaj, J. Appl. Phys. **94**, 7505 (2003).
[18] G. Bentoumi, V. Timoshevskii, N. Madini, M. Côté, R. Leonelli, J.-N Beaudry, P. Desjardins, and R. A. Masut, Phys. Rev. B **70**, 035315 (2004).
[19] P. J. Klar, H. Grüning, W. Heimbrodt, J. Koch, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, Appl. Phys. Lett. **76**, 3439 (2000).
[20] G. Ciatto, H. Renevier, M. G. Proietti, A. Polimeni, M. Capizzi, S. Mobilio, and F. Boscherini, Phys. Rev. B **72**, 085322 (2005).
[21] P. J. Klar, H. Grüning, M. Güngerich, W. Heimbrodt, J. Koch, T. Torunski, W. Stolz, A. Polimeni, and M. Capizzi, Phys. Rev. B **67**, 121206(R) (2003).
[22] M. Bissiri, G. Baldassarri Höger von Högersthal, A. Polimeni, V. Gaspari, F. Ranalli, M. Capizzi, A. Amore Bonapasta, F. Jiang, M. Stavola, D. Gollub, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **65**, 235210 (2001).
[23] A. Polimeni, M. Bissiri, M. Felici, M. Capizzi, I. A. Buyanova, W. M. Chen, H. P. Xin, and C. W. Tu, Phys. Rev. B **67**, 201303(R) (2003).
[24] R. Trotta *et al.* (unpublished).
[25] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Oxford University Press, Oxford, England, 1971).
[26] M. Felici, A. Polimeni, A. Miriametro, M. Capizzi, H. P. Xin, and C. W. Tu, Phys. Rev. B **71**, 045209 (2005).
[27] P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975).
[28] H. Grüning, K. Kohary, S. D. Baranovskii, O. Rubel, P. J. Klar, A. Ramakrishnan, G. Ebbinghaus, P. Thomas, W. Heimbrodt, W. Stolz, and W. W. Rühle, Phys. Status Solidi C **1**, 109 (2004).
[29] The values of w obtained from the fitting procedure are nearly unaffected by the inclusion in the PLE line shape of the states

due to the above-gap continuum; see Fig. 2. As a consequence, contribution from these states was omitted in order to minimize the number of fitting parameters. For the same reason, an equal linewidth was assumed for both the light- and heavy-hole exciton line shapes.

[30] J. S. Blackmore, J. Appl. Phys. **53**, R123 (1982).

[31] F. Masia, G. Pettinari, A. Polimeni, M. Felici, A. Miriametro, M. Capizzi, A. Lindsay, S. B. Healy, E. P. O'Reilly, A. Cristofoli, G. Bais, M. Piccin, S. Rubini, F. Martelli, A. Franciosi, P. J. Klar, K. Volz, and W. Stolz, Phys. Rev. B **73**, 073201 (2006).

[32] The theoretical value depends on the choice of the pseudopotentials used in the calculations (see Ref. 2), which are based on supercells of $GaAs_{1-x}N_x$.

[33] Comparable values of the FE linewidth broadening were reported for similar x values in Ref. 18, though by a different line shape fitting procedure.

[34] This $k \sim 1$ meV contribution adds to the effect of alloy disorder w through $w' = \sqrt{w^2 + k^2}$, but it does not affect substantially our analysis, except for $x_{\text{eff}} \sim 0\%$.

[35] Simone Sanna and Vincenzo Fiorentini, Phys. Rev. B **69**, 125208 (2004).

[36] F. Yang, M. Wilkinson, E. J. Austin, and K. P. O'Donnell, Phys. Rev. Lett. **70**, 323 (1993).

[37] M. Grassi Alessi, F. Fragano, A. Patane', M. Capizzi, E. Runge, and R. Zimmermann, Phys. Rev. B **61**, 10985 (2000).

[38] A. Polimeni, A. Patane', M. Grassi Alessi, M. Capizzi, F. Martelli, A. Bosacchi, and S. Franchi, Phys. Rev. B **54**, 16389 (1996).

[39] M. Gurioli, A. Vinattieri, J. Martinez-Pastor, and M. Colocci, Phys. Rev. B **50**, 11817 (1994).

[40] A. Patane', A. Levin, A. Polimeni, L. Eaves, P. C. Main, M. Henini, and G. Hill, Phys. Rev. B **62**, 11084 (2000).