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Reduced temperature dependence of the band gap in $GaAs_{1-y}N_y$ investigated with photoluminescence

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The effect of the temperature (T) on the band-gap energy (E_g) of hydrogenated $GaAs_{1-y}N_y/GaAs$ quantum wells has been studied by photoluminescence from 10 to 540 K. Nitrogen insertion in GaAs leads to a sizable decrease of E_g and to a flattening of the band-gap dependence on T with respect to that of bare GaAs. Atomic hydrogen irradiation passivates nitrogen in $GaAs_{1-y}N_y$ and leads to an increase of E_g, which is accompanied by an increase in the thermal shrinkage rate (S) of the band gap. Eventually, a strong correlation between S and the concentration of unpassivated N atoms is found. The wide temperature range investigated and the hydrogen induced effects permit to claim that the reduced thermal redshift of the gap in N containing samples: (i) cannot be ascribed to the reduction of the pressure coefficients in Ga(AsN); (ii) can be accounted for, instead, by a cancellation of the Debye-Waller and self-energy terms in the T dependence of the band gap. The latter effect is explained in terms of a recently proposed increase in the localized character of the conduction band edge with increasing N concentration.

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The search for highly efficient light emitters in the 1.3–1.55 μm range compatible with the GaAs technology has led to a renewed interest in the physical properties of (InGa)(AsN)/GaAs heterostructures.[1] Indeed, nitrogen incorporation in (InGa)As results in a giant band-gap bowing of the host lattice for increasing nitrogen concentration.[2] Nitrogen affects also the dependence of the host lattice band gap on external perturbations such as hydrostatic pressure[3–7] and lattice temperature, T.[3,8–16] In both cases a strong deviation from the behavior found in bare (InGa)As is observed. Anomalously small pressure coefficients have been measured by several authors[3–7] and explained in terms of a localized-delocalized mixed character of the (InGa)(AsN) conduction band (CB) edge.[4,17] The temperature dependence of the $In_xGa_{1-x}As_{1-y}N_y$ optical gap shows a pronounced slowing down with respect to that of the N-free material, this effect being larger for $x=0$ and increasing y.[3,8–13] The reduction of the thermal redshift of the band gap in (InGa)(AsN) has been ascribed in Ref. 3 to a decrease of the deformation potentials in N containing material or, in Refs. 10 and 12, it has been explained in the framework of a band anticrossing model.[4] Other authors pointed out the sizable contribution of localized states to the temperature dependence of the photoluminescence (PL) peak energy position for low T's.[8–10,12–16]

Recently, it has been shown that the optical properties of $In_xGa_{1-x}As_{1-y}N_y/GaAs$ quantum wells (QWs) are strongly affected by H irradiation, which leads to a band-gap blueshift of the N containing material.[18] Removal of hydrogen from $In_xGa_{1-x}As_{1-y}N_y$:H restores the optical gap the samples had before hydrogenation. Therefore, the direct effects of H on the (InGa)(AsN) band structure are fully reversible.[19] One may wonder if hydrogen affects to the same extent the dependence of the material's electronic properties on external perturbations. To answer this question we have investigated the temperature dependence of the band gap of hydrogenated $GaAs_{1-y}N_y/GaAs$ single quantum wells. PL measurements carried out from 10 to 540 K show that the rate at which the QW gap redshifts with increasing T can be tuned by post growth hydrogen treatments. As in previous reports,[3,8–13] we find that the thermal shrinkage rate S of the $GaAs_{1-y}N_y$ gap sizably decreases with increasing y. On the contrary, H irradiation leads to an increase in S that correlates well with the amount of electronically active N atoms left in the quantum well. The wide temperature range investigated and the observed hydrogen effects permit to ascribe the reduced temperature dependence of the $GaAs_{1-y}N_y$ band gap mainly to a change in the electron-phonon coupling.

We have studied two $GaAs_{1-y}N_y/GaAs$ single QWs ($y=0.016$ and 0.029) having the same thickness ($L=9.0$ nm) and grown by solid source molecular beam epitaxy. All samples have a 100 nm thick GaAs capping layer. Post growth treatment with atomic hydrogen was obtained by ion-beam irradiation from a Kaufman source with the samples held at 300 °C. The ion energy was about 100 eV and the current density was of the order of few tens of $\mu A/cm^2$. Several hydrogen doses ($d_H=10^{16}–10^{18}$ $ions/cm^2$) have been used in this study. Some of the hydrogenated samples have been annealed for 3 h at 10^{-6} Torr and temperature $T_a=330\,°C$. PL was excited by the 515 nm line of an Ar^+ laser, dispersed by a single 1 m monochromator and detected by a liquid nitrogen cooled Ge detector.

The PL spectra of the untreated QWs are shown in Fig. 1 for different temperatures. The PL band below the GaAs band edge is due to carrier recombination in the $GaAs_{1-y}N_y$ well. The high material quality as well as the QW design

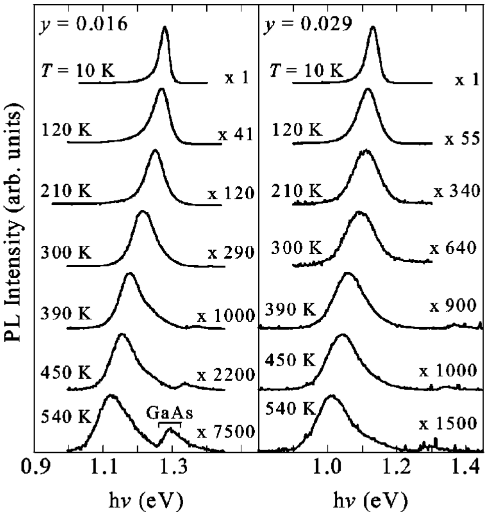

FIG. 1. Peak normalized PL spectra of $GaAs_{1-y}N_y/GaAs$ quantum wells with $y=0.016$ (left panel) and 0.029 (right panel) recorded at different temperatures. Normalization factors are given for each spectrum. Laser power density $P=60\ W/cm^2$.

allow us to measure a PL signal up to temperatures in excess of 500 K. Carrier thermal escape in the $y=0.016$ sample is higher than in the $y=0.029$ sample as shown by the lower signal decrease between $T=10$ and 540 K in the latter sample due to its deeper confining potential. This is confirmed by the higher contribution to the PL signal from the GaAs barrier at high temperatures observed in the shallower QW (see Fig. 1, $y=0.016$). For $T<200$ K, in both samples the PL lineshape has a characteristic low-energy tail due to localized excitons, as extensively reported in previous works.[8–10,12–16] At higher temperatures, the PL lineshape is symmetric and eventually an exponential high-energy tail appears for $T>300$ K due to emission from thermally populated delocalized states of the well. Therefore, two regimes should be distinguished when studying the PL temperature dependence of heterostructures with a high density of localized states, as those investigated here. In the low-temperature range ($T<200$ K), the band-gap reduction is contrasted by the thermally activated detrapping of localized excitons toward the conduction band states and the material band gap seems to slow down or even blueshift with increasing temperature.[8–10,12–16] Once all the localized excitons have been ionized ($T>200$ K), the T dependence of the PL peak position follows closely that found for the gap on the ground of absorptionlike measurements.[12] In this work we will focus on this high-temperature regime.

The shift R_S of the PL peak position normalized to its $T=10$ K value is shown as a function of temperature in Fig. 2 for different y values.[20] The $y=0$ data have been measured in one of the investigated samples. First, we note that at fixed temperature R_S sizably decreases with increasing N concentration. We quantify this effect by the thermal shrinkage rate S of the $GaAs_{1-y}N_y$ gap. If we disregard localization effects by measuring the slope of R_S for $T\geqslant 300$ K, S is equal to 0.48, 0.37, and 0.32 meV/K for $y=0$, 0.016, and 0.029, respectively. In Refs. 10 and 12, the slowing down of the thermal shrinkage of the (InGa)(AsN) gap has been modeled in terms of a band anticrossing model.[4] Therein, the authors pointed out that an increase in y results in an increasing localized character of the CB edge and, therefore, in an increased T insensitivity of the (InGa)(AsN) gap. In Ref. 3, on the other hand, the above effects have been explained in terms of a decrease in the energy gap deformation potential in the N containing samples.

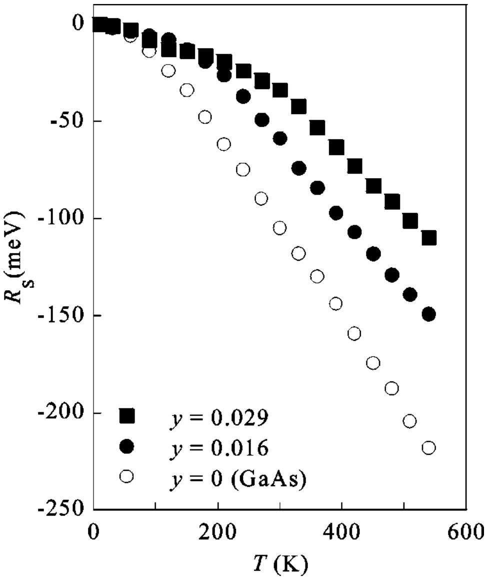

FIG. 2. Shift, R_S, of the PL peak position normalized to its $T=10$ K value vs temperature for different nitrogen concentration y, $y=0$ data have been measured in one QW sample.

The temperature dependence of the band gap E_g can be written as

$$\frac{dE_g}{dT}=\left(\frac{\partial E_g}{\partial T}\right)_l+\left(\frac{\partial E_g}{\partial T}\right)_{\text{el-ph}}, \tag{1}$$

where the first and second term on the right-hand side account for the T variation of E_g caused by the lattice thermal expansion and electron-phonon interaction, respectively.[21] Moreover, $(\partial E_g/\partial T)_l=-3B\alpha(\partial E_g/\partial P)_T$, where B, α, and P are the crystal bulk modulus, thermal expansion coefficient, and applied pressure, respectively. One can reasonably assume that the elastic and thermal properties (i.e., B and α) of the host lattice do not change much upon introduction of a small amount of N such as that present in our samples. On the contrary, in the range of pressure of interest to us (ambient pressure) the pressure coefficient $(\partial E_g/\partial P)_T$ is about 60 meV/GPa for $y=0.015$–0.023, that is half the value found in GaAs (110 meV/GPa).[3–5,7] On the ground of Refs. 3 and 22, this reduction of the pressure coefficient found in (InGa)(AsN) accounts for no more than 10–15% of the band-gap thermal shrinkage. Therefore, the reduction of R_S shown in Fig. 2, namely, more than 50% on going from GaAs to $GaAs_{0.971}N_{0.029}$, cannot be accounted for solely by lattice thermal expansion arguments. We will discuss in the following the second term in Eq. (1), $(\partial E_g/\partial T)_{\text{el-ph}}$, which deals with the electron-phonon interaction.

Let us now consider the effect of temperature on the band gap of hydrogenated $GaAs_{1-y}N_y$ quantum wells. Figure 3

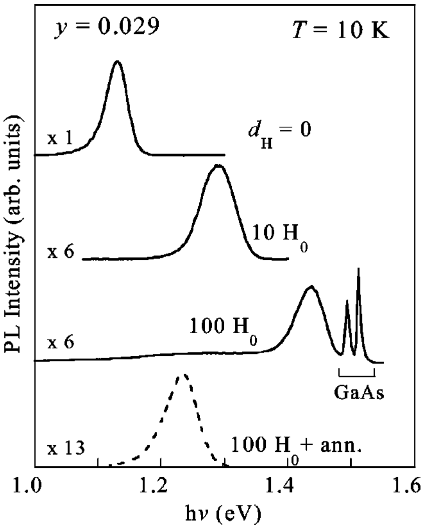

FIG. 3. Peak normalized PL spectra (solid lines) of the $GaAs_{0.971}N_{0.029}$ QW irradiated with different hydrogen doses d_H ($H_0 = 10^{16}$ ions/cm^2). Dashed line is a PL spectrum of the $d_H = 100\ H_0$ sample annealed at 330 °C for 3 h. Normalization factors are given for each spectrum. Laser power density $P = 60$ W/cm^2.

shows the PL spectra (solid lines) of the $y = 0.029$ QW for different H irradiation doses. For increasing d_H, the well band gap blueshifts toward the GaAs gap and it pins to an energy about 80 meV below that of the GaAs band gap at the highest d_H values. In the same d_H range, the PL peak position of the $y = 0.016$ sample pins to about 30 meV above that of the $y = 0.029$ sample (this finding will be discussed in the following). Annealing the hydrogenated sample ($d_H = 10^{18}$ ions/cm^2) at 330 °C for 3 h results in a redshift of the gap (dashed line in Fig. 3). No clear dependence of the PL linewidth on H dose is found, despite H passivates N. This indicates that the disordered character of the QW potential is mostly due to interface roughness and alloy disorder, which are not affected by hydrogenation. Therefore, insertion (removal) of H leads to a decrease (increase) in the material effective N concentration, and, in turn, to an increase (decrease) in the band gap. On the ground of first-principles density functional calculations in a supercell approach, the H-induced passivation of N can be attributed to the formation of stable N-H_n complexes.[23] Indeed, preliminary far-infrared absorption measurements show that a new N-H local vibrational mode appears at 3195 cm^{-1} as a result of the bonds formed by H at its equilibrium position in the lattice.[23] The observation of this mode has been reported also in unintentionally H-containing Ga(AsN) epilayers[24] and ZnSe:N compounds.[25]

Figures 4(a) and 4(b) show the shift of the PL peak position relative to $T = 10$ K as a function of T for different H doses in the case of $y = 0.016$ and 0.029, respectively. The experimental T variation of the GaAs band gap is shown by open circles (same data of Fig. 2). For both $y = 0.016$ and 0.029 samples, hydrogen affects the rate at which the $GaAs_{1-y}N_y$ gap redshifts. In fact, R_S increases with increasing H dose and, finally, its temperature dependence approaches that of the GaAs gap.[26] Hydrogen, therefore, deeply affects the Ga(AsN)/GaAs electronic properties as well as their change under external perturbations. Moreover, the removal of H leads to a recovery of the $GaAs_{1-y}N_y$ thermal properties, as shown in Fig. 4(b) by the $d_H = 10^{18}$ ions/cm^2 annealed sample (full triangles). In this case, an intermediate behavior between the GaAs and the hydrogen free $GaAs_{0.971}N_{0.029}$ QW is found. Therefore, the shift of the band gap with temperature is determined ultimately by the *effective* N concentration in the QW. This latter is given by the number of N atoms incorporated in the sample minus those passivated by H irradiation and its value can be estimated by that of the QW band gap at $T = 300$ K, E_g(RT). Figure 5 shows the thermal shrinkage rate S of the gap vs E_g(RT) for two samples with different as grown N concentrations and post growth treatments. For both samples S and E_g(RT) are strongly correlated. The two set of data are rigidly shifted along the x axis one respect to the other by about 45 meV. This offset can be in large part explained as follows. N introduction in the GaAs lattice affects the host E_g by two concomitant effects. The first is the N induced anticrossing/mixing of the states of the host material conduction band as it has been discussed in Refs. 4 and 17. The second, hitherto neglected effect is the tensile strain at the GaAs/$GaAs_{1-y}N_y$

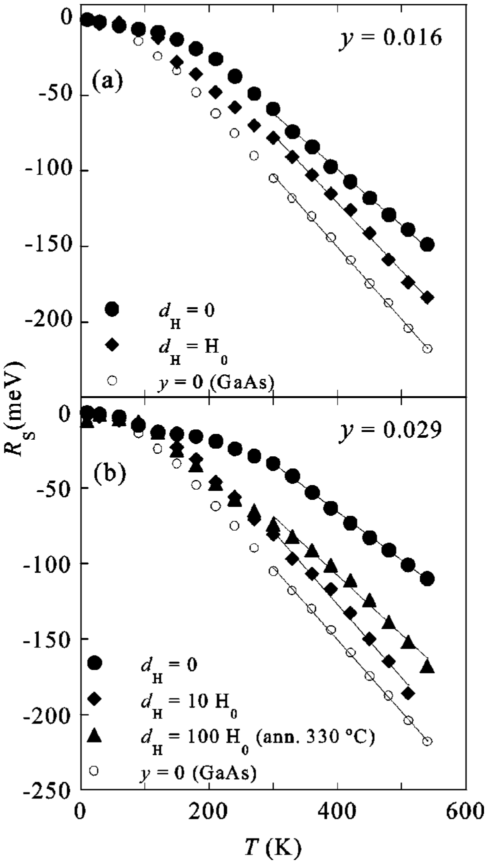

FIG. 4. (a) Shift, R_S, of the PL peak position normalized to its $T = 10$ K value vs temperature for the $y = 0.016$ sample treated with different H doses d_H ($H_0 = 10^{16}$ ions/cm^2). The open circles are the same GaAs data shown in Fig. 2. Solid lines are linear best fit to the data in the T range from 300 to 540 K. (b) The same as in (a) for the $y = 0.029$ sample. The full triangles refer to the $d_H = 100\ H_0$ sample annealed at 330 °C for 3 h.

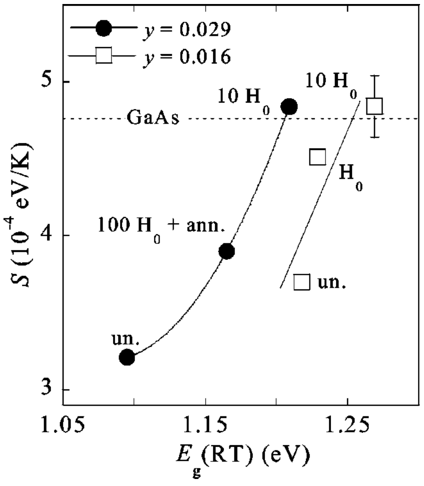

FIG. 5. Thermal shrinkage rate of the gap S (measured by the slope of the PL peak position vs T for $T \geqslant 300$ K), as a function of the QW band gap at $T = 300$ K, E_g(RT). Different symbols refer to different y. For each point the hydrogen dose d_{H} ($\mathrm{H}_0 = 10^{16}$ ions/cm^2) is indicated. "un." stands for untreated material; "ann." stands for hydrogenated sample annealed at 330 °C for 3 h. Solid lines are guides to the eye. The horizontal dashed line indicates the S value for bulk GaAs. An estimate of the error bar is also shown.

interfaces.[27] This strain, which increases with the total amount of N in the well, should neither affect sizably the T dependence of the material band gap[28] nor change too much upon H irradiation of the material. Therefore, once all N atoms have been passivated by H, the different $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ QWs are substantially equivalent to GaAs layers under different tensile strains. The tensile strain contribution to the band gap of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ grown on GaAs can be estimated similarly to what reported for (InGa)As/(AlGa)As heterostructures.[29] In the present $\mathrm{GaAs}_{1-y}\mathrm{N}_y$/GaAs case, we use a Vegard's interpolation between the lattice parameters, deformation potentials, and elastic constants of GaAs and cubic GaN.[30] We find an energy difference of 37 meV between the band gap of the $y = 0.016$ and $y = 0.029$ samples due to tensile strain. This value agrees well with the rigid shift of 45 meV exhibited by the data shown in Fig. 5, as well as with the 30 meV difference between the saturation values with d_{H} of the PL peak of the $y = 0.016$ and 0.029 samples.

Some conclusions can be drawn on the basis of the here reported effects that H irradiation has on the T dependence of the $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ band gap. Hydrogen affects the electronic but not the lattice properties of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$, at least at a very first approximation. Therefore, the slowdown of the thermal shrinkage of the $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ band gap should be of electronic origin, namely, N (and H) affects the electron-phonon coupling term in Eq. (1). Debye-Waller and self-energy terms contribute to $(\partial E_g/\partial T)_{\text{el-ph}}$ and give rise to a shift of the gap to lower and higher energies with increasing temperature, respectively.[21,22] Following Ref. 31, a cancellation of the Debye-Waller and self-energy contributions may take place for narrow energy bands such as those of impurities with wave functions strongly localized in real space. In this limit, neighboring orbitals overlap negligibly and $(\partial E_g/\partial T)_{\text{el-ph}}$ tends to zero.[31] In the present case of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$, the localization degree of the conduction band edge has been described by different models. In Ref. 4, a band anticrossing between a N induced level and the GaAs CB leads to a free/localized mixed character of the electron wave function, which accounts for the pressure and temperature dependence of the $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ band gap.[4,11,12] In a recent comprehensive work, Kent and Zunger have estimated the evolution of the electronic structure of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ for increasing y.[17] These authors predict a gradual, sizable decrease of the Γ character of the CB edge in Ga(AsN), which occurs for concentrations $y = 0.02-0.04$ because of a mixing between N cluster localized states and N perturbed conduction band states. This evolution is accompanied by an increase in the electron effective mass and by a lower temperature coefficient of Ga(AsN) relative to GaAs, as found in the present work. Therefore, due to the diminished overlap between the electronic wave functions the Debye-Waller and self-energy terms tend to cancel out in the T dependence of the $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ gap, with an ensuing decrease in the thermal gap shrinkage.

In conclusion, we have measured the photoluminescence properties of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$/GaAs quantum wells over a wide temperature range ($T = 10-540$ K) and for different degrees of N passivation by H. This has allowed us to address the mechanism responsible for the slower band-gap reduction with T usually found in N containing materials. Such mechanism relies on an increasing localized character of the electron wave function for increasing N concentration, which leads to a cancellation between the Debye-Waller and self-energy terms in the T dependence of the $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ gap.

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[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys. **35**, 1273 (1996).

[2] For a review see, I.A. Buyanova, W.M. Chen, and B. Monemar, MRS Internet J. Nitride Semicond. Res. **6**, 2 (2001) (http://nsr.mij.mrs.org/6/2/).

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

[4] 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).

[5] 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).

[6] 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).

[7] M.S. Tsang, J.N. Wang, W.K. Ge, G.H. Li, Z.L. Fang, Y. Chen, H.X. Han, L.H. Li, and Z. Pan, Appl. Phys. Lett. **78**, 3595 (2001).

[8] J.C. Fan, W.K. Hung, Y.F. Chen, J.S. Wang, and H.H. Lin, Phys. Rev. B **62**, 10 990 (2000).

[9] L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vannuffel, A. Million, and A. Chevanes-Paule, Appl. Phys. Lett. **76**, 2241 (2000).

[10] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Appl. Phys. Lett. **77**, 2870 (2000).

[11] I. Suemune, K. Uesugi, and W. Walukiewicz, Appl. Phys. Lett. **77**, 3021 (2000).

[12] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 195320 (2001).

[13] M.-A. Pinault and E. Tournié, Appl. Phys. Lett. **78**, 1562 (2001).

[14] A. Kaschener, T. Lüttgert, H. Born, A. Hoffmann, A. Yu. Egorov, and H. Riechert, Appl. Phys. Lett. **78**, 1391 (2001).

[15] S. Shirakata, M. Kondow, and T. Kitatani, Appl. Phys. Lett. **79**, 54 (2001).

[16] X.D. Luo, Z.Y. Xu, W.K. Ge, Z. Pan, L.H. Li, and Y.W. Lin, Appl. Phys. Lett. **79**, 958 (2001).

[17] P.R.C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).

[18] A. Polimeni, G. Baldassarri H.v.H., M. Bissiri, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 201304 (2001).

[19] G. Baldassarri H.v.H., M. Bissiri, A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Appl. Phys. Lett. **78**, 3472 (2001).

[20] In the analysis of the temperature dependence of the gap energy we neglect the variation of the QW potential offset due to the different thermal variation of the well and barrier material band gaps. In fact, the change of carrier confinement energy between 10 K and 540 K produced by this effect is quite small (∼5 meV).

[21] P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983).

[22] C.K. Kim, P. Lautenschlager, and M. Cardona, Solid State Commun. **59**, 797 (1986).

[23] M. Bissiri *et al.* (unpublished).

[24] S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, and N. Karam, Appl. Phys. Lett. **78**, 748 (2001).

[25] J.A. Wolk, J.W. Ager III, K.J. Duxstad, E.E. Haller, N.R. Taskar, D.R. Dorman, and D.J. Olego, Appl. Phys. Lett. **63**, 2756 (1993); A. Kamata, H. Mitsuhashi, and H. Fujita, *ibid.* **63**, 3353 (1993).

[26] The $d_{\mathrm{H}}=10$ H_0 ($y=0.016$) and $d_{\mathrm{H}}=100$ H_0 ($y=0.029$) samples are not shown in Figs. 4(a) and 4(b), respectively, for clarity purposes. In fact, their R_S values overlap those found for GaAs.

[27] I.A. Buyanova, G. Pozina, P.N. Hai, W.M. Chen, X.P. Xin, and C. W. Tu, Phys. Rev. B **63**, 033303 (2001).

[28] A. Patanè, A. Levin, A. Polimeni, F. Schindler, L. Eaves, P.C. Main, and M. Henini, Appl. Phys. Lett. **77**, 2979 (2000).

[29] S.-C. Hong, G.P. Kothiyal, N. Debbar, P. Bhattacharya, and J. Singh, Phys. Rev. B **37**, 878 (1988).

[30] I. Vurgaftman, J.R. Meyer, and L.R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).

[31] P. Allen and V. Heine, J. Phys. C **9**, 2305 (1976).