Carrier thermalization within a disordered ensemble of self-assembled quantum dots

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The electroluminescence (EL) and photocurrent (PC) spectra of *p-i-n* structures containing $In_xGa_{1-x}As/GaAs$ self-assembled quantum dots (QD's) are studied from 10 to 290 K. Comparison between the EL and PC shows a Stokes Shift, i.e., the QD emission is redshifted with respect to the QD absorption in PC. The magnitude of the Stokes Shift depends on the temperature and on the extent of the dot energy dispersion, as measured by the QD absorption linewidth in different samples. The origin of the Stokes shift is discussed in terms of carrier thermalization effects by analogy with carrier distribution in disordered quantum wells.

I. INTRODUCTION

Since the first investigation of self-assembled quantum dots (QD's), there has been a great deal of interest in the physics of these systems and in potential applications, such as the quantum dot laser.[1] Despite years of intensive research, there are still several problems hindering the exploitation of the zero-dimensional properties of the dots. These include the control of the uniformity and ordering of the dots as well as the realization of a ''pure'' zero-dimensional structure. In particular, of prime importance is the question of whether the dots are uncoupled or coupled in the growth plane. Alternatively, can the dots be best described as localization centers in the potential profile of the two-dimensional wetting layer that forms beneath them? There is currently no clear answer to this question. Several experiments have demonstrated the zero-dimensional nature of carrier confinement in the dots;[2–5] on the other hand, similarities with disordered quantum wells (QW's) can be found. Luminescence experiments with local-probe techniques have provided evidence of localized excitons in quantum wells with an atomlike density of states. Carrier localization occurs in the local energy minima of the fluctuating QW potential due to the interfacial and compositional disorder.[6–11]

In this paper, we present a systematic study of carrier redistribution in $In_xGa_{1-x}As/GaAs$ QD's by comparison of electroluminescence (EL) and photocurrent (PC) measurements. Despite previous work dealing with the emission and absorption spectroscopy in QD's,[1] little attention has been devoted to a comparison of the two types of measurement.[12,13] We show the existence of a redshift of the QD emission in EL with respect to the QD absorption in PC, referred to as the Stokes shift, *SS*. *SS* depends on the linewidth of the QD absorption spectrum and on temperature. The data are explained in terms of a thermal redistribution of carriers between dots by analogy with carrier thermalization in disordered quantum wells.[14–17]

II. EXPERIMENT

The samples are *p-i-n* structures grown by molecular beam epitaxy on n^+ GaAs substrates. The growth scheme is the following: a 0.7-μm-thick n^+-doped GaAs buffer layer (n^+:$4\times10^{18}\,cm^{-3}$) followed by a 0.1-μm-thick *n*-doped GaAs (n:$4\times10^{16}\,cm^{-3}$); an undoped, intrinsic region (*i*), which consists, respectively, of a 0.1-μm-thick GaAs layer, an $In_xGa_{1-x}As$ layer, and a 60-nm-thick GaAs layer; finally, the growth is completed by a 0.5-μm-thick p^+-doped GaAs layer (p^+:$2\times10^{18}\,cm^{-3}$). The structures were grown at 600 °C except for the $In_xGa_{1-x}As$ layer and the overgrown GaAs cap layer, which were both grown at 450 or 500 °C to avoid In segregation and desorption effects. Several structures were examined, varying in the In content of the $In_xGa_{1-x}As$ ($x=0.5$ and 1), in the $In_xGa_{1-x}As$ layer thickness L or in the GaAs substrate orientation [(311)*B* or (100)]. L is equal to 1.3, 1.8, or 2 monolayers (ML) for $x=1$ and equal to 1.1 or 1.4 nm for $x=0.5$. The variety of growth conditions allows us to study both wetting layer (WL) ($x=1$ and $L=1.3$ ML) and QD structures ($L=1.8$ or 2 ML for $x=1$, and $L=1.1$ or 1.4 nm for $x=0.5$) with correspondingly different carrier-confining potentials and morphologies. The dot formation was controlled *in situ* by monitoring the reflection high-energy electron-diffraction pattern. The dot morphology was studied by atomic force microscopy on samples having a similar growth scheme but with the growth terminated after the $In_xGa_{1-x}As$ layer.[18] The dots have a density of $\sim10^{11}\,cm^{-2}$, a mean diameter of ~20–30 nm, and a mean height of ~1–2 nm. The *p-i-n* structures were processed into circular mesas, 200 μm in diameter. A ring-shaped electrical contact was fabricated on top of the mesa to permit optical access to the sample. This type of structure allows us to compare the emission (EL) and the absorption (PC) of the same device, thus avoiding any problems of nonhomogeneity. In particular, the PC technique provides a sensitive tool for probing the absorption of a single QD layer, which is too weak to be detected in a transmission measurement. The EL was dispersed by a $\frac{3}{4}$ m monochromator and detected by a cooled Ge or (InGa)As diode. For PC measurements, a tungsten-halogen lamp dispersed by a 0.25 m monochromator was used as excitation source and the photocurrent signal was measured using a standard lock-in technique. The PC spectra were measured under reverse bias (positive-biased substrate) with an applied voltage

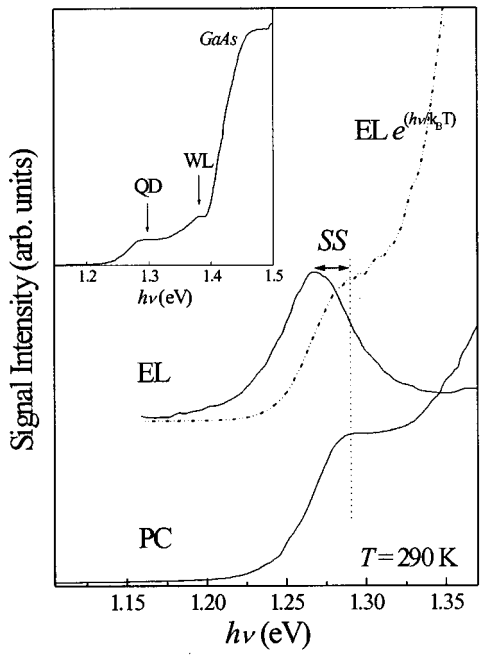

FIG. 1. Electroluminescence (EL) and photocurrent (PC) spectra at room temperature ($T=290$ K) for $In_{0.5}Ga_{0.5}As$ quantum dots grown on a (100) GaAs substrate with $L=1.1$ nm. The EL spectrum is measured under a current of 70 mA. The PC spectrum is measured with an applied voltage $V=-1$ V. The dotted line represents the curve $L(h\nu)e^{h\nu/k_BT}$, where $L(h\nu)$ is given by the EL spectrum. *SS* is the Stokes shift of the dot EL spectrum with respect to the dot fundamental absorption in PC. The inset shows the PC spectrum in an extended energy range.

$V=0$ or -1 V. In this voltage range, the PC spectra are almost independent of the bias conditions.

III. RESULTS AND DISCUSSION

Figure 1 shows the EL and PC spectra at room temperature ($T=290$ K) for $In_{0.5}Ga_{0.5}As/GaAs$ quantum dots grown on a (100) GaAs substrate with $L=1.1$ nm. The EL spectrum shows a band around 1.27 eV due to electron-hole pair recombination from the ground state of the dots. A similar band is observed in the PC spectrum, but shifted to higher energy with respect to the EL and attributed to the fundamental dot absorption. Finally, on the high-energy side of the PC spectrum (see the inset of Fig. 1) we observe two more features. They are due to absorption of the $In_{0.5}Ga_{0.5}As$ wetting layer (WL) and the intrinsic absorption edge of the GaAs matrix. The unambiguous assignment of these resonances follows from a comparison of the PC spectra of *p-i-n* structures with and without the $In_xGa_{1-x}As$ layer.

Of particular interest is the large energy shift (~ 20 meV) between the QD EL spectrum and the QD fundamental absorption in PC, referred to as the Stokes shift. A similar observation has been previously reported by comparison of photoluminescence (PL) and PC (Ref. 12) or photovoltage[13] measurements at room temperature, and tentatively explained in terms of a preferential tunneling of carriers out of the dots from the higher energy states, which results in a blueshift of the QD PC with respect to the absorption and PL of the dots.[12] However, recent PC measurements in QD structures showed that the above effect is relevant only at low temperatures (<150 K) and that even for these cases the energy deviation of the PC from the absorption is small (<8 meV).[19] In light of these considerations, we propose that a different mechanism is responsible for the observed large *SS*.

By analogy with the optical properties of QW systems,[14–17] we propose that the *SS* may indicate a thermalization of carriers within the energy state distribution of the dots. In conventional QW's, interface and compositional disorder generates a fluctuating QW potential that leads to an inhomogeneous broadening of the spectral lines. Carrier redistribution between the states of the QW depends on temperature.[14] Carriers are assumed to be in thermal equilibrium, with a Boltzmann distribution characterized by an effective carrier temperature T_c. Then the emission spectrum (L) is related to the absorption spectrum α by the relation[14]

$$L(h\nu)\sim\alpha(h\nu)e^{-h\nu/k_BT_c}, \tag{1}$$

where $h\nu$ is the photon energy and k_BT_c is the carrier thermal energy. By considering a Gaussian profile for the exciton fundamental absorption $\alpha_o(h\nu)$ it can be shown that $L(h\nu)$ is redshifted with respect to $\alpha_o(h\nu)$ by the amount[14]

$$SS=0.18\frac{W^2}{k_BT_c}, \tag{2}$$

where W is the full width at half maximum of $\alpha_o(h\nu)$.

We applied the above model to the data at room temperature from our QD samples. In this case carrier transfer between the dots occurs through carrier diffusion in the wetting layer (WL) and in the GaAs barriers. Carriers thermally escape from the dots to the delocalized states of the WL and GaAs matrix.[20–24] Subsequently, they redistribute in the growth plane according to the Boltzmann distribution by diffusing from the high-energy to the low-energy dot states. This results in a Stokes shift of the emission of the dots with respect to their fundamental absorption in PC. We simulated the QD absorption $\alpha(h\nu)$ by the curve $L(h\nu)e^{h\nu/k_BT}$, where $L(h\nu)$ is the emission spectrum measured by EL, and we assumed that carriers obey Boltzmann statistics at the lattice temperature $T=290$ K. As shown by the dotted line in Fig. 1, this curve has a similar line shape to the PC spectrum in the region of the fundamental absorption of the dots.

The above discussion implies that the *SS* is related to the degree of carrier thermalization, as measured by the ratio between the carrier thermal energy (k_BT_c) and the inhomogeneous broadening of the QD absorption band W. We measured the *SS* for samples with different W. In order to define *SS*, first we studied the dependence of the QD EL spectra on the number of injected carriers, as measured by the current through the device. For each sample in the investigated current range of 1–10 to 100 mA, the peak energy position of the QD EL band is almost independent of the excitation conditions. This makes the value of *SS* a well-defined quantity at room temperature. As shown in Fig. 2 for samples with different W, *SS* and W are strongly correlated; larger W means

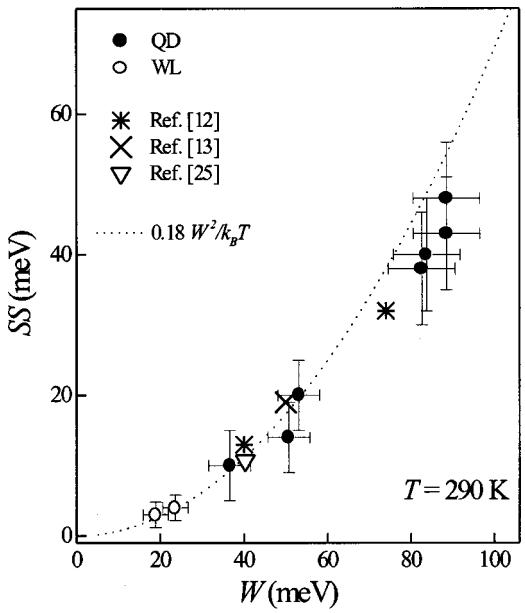

FIG. 2. Stokes shift *SS* of the dot (OD: full dots) and wetting layer (WL: open dots) EL band vs the fundamental absorption linewidth $W(T=290\,\mathrm{K})$. The error bars take into account the uncertainty in the determination of *SS* and *W*, as derived from fits to the PC spectra. The star, cross, and triangle symbols are the data from Refs. 12, 13, and 25, respectively. The continuous line is the curve $SS=0.18W^2/k_BT$.

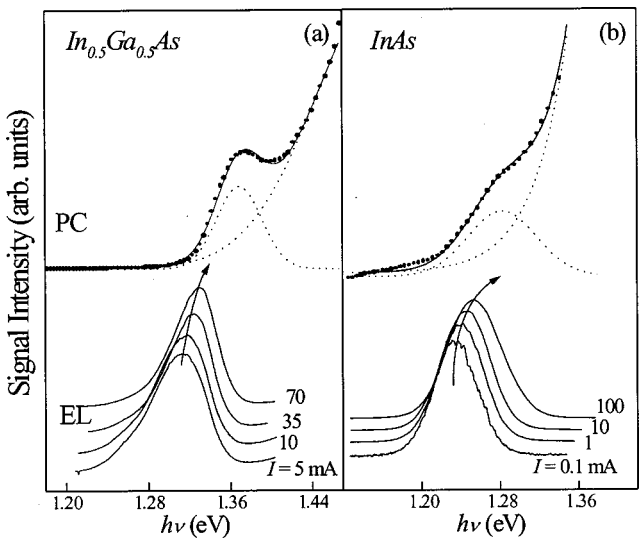

FIG. 3. Low-temperature (10 K) electroluminescence (EL) spectra as a function of current *I* for (a) $In_{0.5}Ga_{0.5}As$ and (b) InAs self-assembled quantum dots (QD's). The arrows indicates the blueshift of the QD EL band with increasing *I*. The photocurrent (PC) spectra of the two samples are plotted in the upper parts of (a) and (b). The continuous line is a fit to the PC data by Gaussian line shapes (dashed lines).

larger *SS*. The same correlation also holds for structures containing a disordered QW, in our case an InAs WL (i.e., no dots), and for self-assembled[12–13,25] or colloidal[26] quantum dots reported in the literature by other groups. The values of the *SS* for two WL samples and those reported in the literature for $In_xGa_{1-x}As$ QD's are plotted in Fig. 2. The *SS* increases with *W* in good agreement with the relation $SS=0.18W^2/k_BT_c$ predicted by the thermalization model (see the dotted line in Fig. 2). The smallest values of the *SS* are found in systems with the narrowest PL linewidth. In particular, *SS* tends to zero for $W\rightarrow 0$, as expected in the limit of perfectly homogeneous QW or in the case of an ensemble of identical dots.

In order to reveal the degree of carrier thermalization at different temperatures, we studied the temperature dependence of the *SS*. When we lower the temperature from 290 to 10 K, we continue to observe a finite *SS* in all samples. In particular, in the regime of low temperature (<200 K), the peak energy position of the QD EL band, and hence the magnitude of the *SS*, depends strongly on the number of injected carriers.

Figures 3(a) and 3(b) show the 10 K EL and PC spectra of $In_{0.5}Ga_{0.5}As$ QD's and InAs QD's, respectively. In both samples, the EL spectra, recorded at different currents *I*, are redshifted with respect to the PC. In particular, the *SS* decreases with increasing *I*. Similar effects are observed by considering the QD photoluminescence spectra monitored as a function of the optical excitation power. These data indicate that for small carrier densities, carriers preferentially relax to the lowest dot energy states. Then, as the carrier density increases further, carriers redistribute in the growth plane and spread over the full QD density of states, thus resulting in a blueshift of the luminescence spectra and a decreasing value of *SS*.

Figure 4 shows the current dependence of *SS* at different temperatures for the sample of Fig. 3(a). The data show that *SS* depends on the excitation conditions used for the EL measurements for $T<200$ K and that *SS* increases with decreasing *T*. The temperature dependence of the *SS* under different currents is shown in the inset of Fig. 4 and compared with that expected by the theoretical curve $SS=0.18W^2/k_BT_c$, with $T_c=T$ and a constant value for *W*. This comparison shows a deviation of the data from the model in the temperature range 10–150 K.

The increasing value of *SS* with decreasing *T* is in qualitative agreement with the thermalization model, but represents a surprising result for a QD system. With decreasing *T*, the thermal coupling between the dots becomes weaker.[21–24] The subsequent suppression of carrier hopping between adjacent dots should prevent carrier redistribution, leading to an approximately random population of the dot levels across the full QD spectrum and a vanishing *SS*. The observation of a Stokes shift at low lattice temperature indicates that carriers are not randomly distributed and that a partial thermalization occurs. This may occur through tunneling between neighboring dots.[27] Alternatively, the wetting layer could still represent an efficient channel for the interdot carrier transfer at low temperature. In fact, an efficient energy exchange between the dots and the wetting layer can always occur by Auger like mechanisms.[28–30]

A quantitative determination of the *SS* at low lattice temperature is not straightforward. This is in general true also for highly disordered QW's, where the *SS* is strongly controlled by the competition between carrier diffusion in the

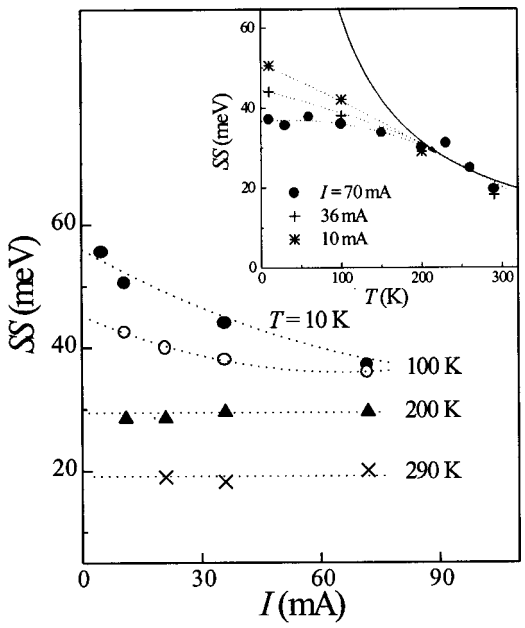

FIG. 4. Current, *I*, dependence of the Stokes Shift, *SS*, measured at different temperatures for $In_{0.5}Ga_{0.5}As$ quantum dots grown on (100) GaAs substrate and $L=1.1$ nm. The inset shows the temperature dependence of *SS* at different *I*. The continuous line is the curve $SS=0.18W^2/k_BT_c$, with $T_c=T$ and $W=50$ meV, and the dotted lines are guides to the eye.

growth plane and the recombination of carriers.[16,17] In particular, due to the high disorder present in QD systems, it seems likely that only a partial thermalization can occur. Also a model for the *SS* at low *T* should include a description of band filling mechanisms, which are responsible for the observed dependence of the *SS* on carrier density (see Fig. 4). As the carrier density increases, the lowest dot energy states are saturated and the carrier population spreads over a larger range of the QD density of states, thus resulting in a decreasing value of *SS*. This behavior is not observed in the regime of high *T*, in which the EL spectrum shifts in energy closer to the maximum absorption of the dots and the importance of band filling mechanisms becomes smaller.

The efficiency of the interdot carrier transfer depends on the dot properties. It is larger in samples with a high dot density and/or with a shallow dot confining potential.[24] In our structures the distance between nearest neighbor dots is small ($\sim$30 nm corresponding to a dot density of $\sim 10^{11}\,cm^{-2}$), the dot energy levels are shallow (the carrier confinement energies are $\sim$ 100 meV),[31] and a wetting layer always forms beneath the dots, representing an efficient channel for the interdot carrier transfer. Of course, because of the large variety of QD structures reported in the literature, a general picture for carrier thermalization within an ensemble of disordered QD's requires a detailed consideration of the dot morphology.

IV. CONCLUSIONS

We studied the EL and PC spectra of *p-i-n* structures containing $In_xGa_{1-x}As/GaAs$ QD's. A comparison between EL and PC spectra at low and room temperature shows that the QD emission is redshifted with respect to the QD absorption. The resulting Stokes shift of the QD emission indicates a carrier thermalization in the growth plane. At room temperature, the *SS* is related to the degree of carrier thermalization, as measured by the ratio between the carrier thermal energy and the inhomogeneous broadening of the QD absorption band, and is well described by analogy with the carrier thermalization in disordered QW's.[14] At low temperature the observation of a nonvanishing Stokes shift and of a strong dependence of the QD luminescence spectra on carrier density indicates the persistence of a strong coupling between neighboring dots.

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[1] D. Bimberg, M. Grundmann, and N. N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, New York, 1999), and references therein.
[2] J. Y. Marzin, J. M. Gérard, A. Izraël, D. Barrier, and G. Bastard, Phys. Rev. Lett. **73**, 716 (1994).
[3] M. Grundmann, J. Christen, N. N. Ledentsov, J. Böhrer, D. Bimberg, S. S. Ruvimov, P. Werner, U. Ritcher, U. Gösele, J. Heydenreich, V. M. Ustinov, A. Yu. Egorov, A. E. Zhukov, P. S. Kop'ev, and Zh. I. Alferov, Phys. Rev. Lett. **74**, 4043 (1995).
[4] Y. Toda, S. Shinomori, K. Suzuki, and Y. Arakawa, Appl. Phys. Lett. **73**, 517 (1998).
[5] A. Chavez-Pirson, J. Temmyo, K. Kamada, H. Gotoh, and H. Ando, Appl. Phys. Lett. **72**, 3494 (1998).
[6] Q. Wu, R. D. Grober, D. Gammon, and D. S. Katzer, Phys. Rev. Lett. **83**, 2652 (1999).
[7] H. F. Hess, E. Betzig, T. D. Harris, L. N. Pfeiffer, and K. W. West, Science **264**, 1740 (1994).
[8] A. Zrenner, L. V. Butov, M. Hagn, G. Abstreiter, G. Bohm, and G. Weimann, Phys. Rev. Lett. **72**, 3382 (1994).
[9] K. Brunner, G. Abstreiter, G. Böhm, G. Tränkle, and G. Weimann, Appl. Phys. Lett. **64**, 3320 (1994).
[10] D. Gammon, E. S. Snow, B. V. Shanabrook, D. S. Katzer, and D. Park, Phys. Rev. Lett. **76**, 3005 (1996).
[11] N. H. Bonadeo, J. Erland, D. Gammon, D. Park, D. S. Katzer, and D. G. Steel, Science **282**, 1473 (1998).
[12] L. Chu, M. Arzberger, A. Zrenner, G. Böhm, and G. Abstreiter, Appl. Phys. Lett. **75**, 2247 (1999).
[13] B. Q. Sun, Z. D. Lu, D. S. Jiang, J. Q. Wu, Z. Y. Xu, Y. Q. Wang, J. N. Wang, and W. K. Ge, Appl. Phys. Lett. **73**, 2657 (1998).
[14] M. Gurioli, A. Vinattieri, J. Martinez-Pastor, and M. Colocci, Phys. Rev. B **50**, 11 817 (1994).
[15] A. Polimeni, A. Patanè, M. Grassi Alessi, M. Capizzi, F. Martelli, A. Bosacchi, and S. Franchi, Phys. Rev. B **54**, 16 389 (1996).
[16] A. Ait-Ouali, J. L. Brebner, R. Y. F. Yip, and R. A. Masut, J. Appl. Phys. **86**, 6803 (1999).

[17] M. Grassi Alessi, F. Fragano, A. Patanè, M. Capizzi, E. Runge, and R. Zimmermann, Phys. Rev. B **61**, 10 985 (2000).
[18] A. Polimeni, M. Henini, A. Patanè, L. Eaves, P. C. Main, and G. Hill, Appl. Phys. Lett. **73**, 1415 (1998); A. Polimeni, A. Patanè, M. Henini, L. Eaves, and P. C. Main, J. Cryst. Growth **201/202**, 276 (1999).
[19] P. W. Fry, I. E. Itskevich, D. J. Mowbray, M. S. Skolnick, J. J. Finley, J. A. Barcher, E. P. O'Reilly, L. R. Wilson, I. A. Larkin, P. A. Maksym, M. Hopkinson, M. Al-Khafaji, J. P. R. David, A. G. Cullis, G. Hill, and J. C. Clark, Phys. Rev. Lett. **84**, 733 (2000).
[20] A. Patanè, A. Polimeni, P. C. Main, M. Henini, and L. Eaves, Appl. Phys. Lett. **75**, 814 (1999).
[21] L. Brusaferri, S. Sanguinetti, E. Grilli, M. Guzzi, A. Bignazzi, F. Bogani, L. Carraresi, M. Colocci, A. Bosacchi, P. Frigeri, and S. Franchi, Appl. Phys. Lett. **69**, 3354 (1996).
[22] H. Lee, W. Yang, and P. C. Sercel, Phys. Rev. B **55**, 9757 (1996).
[23] Y. Tang, D. H. Rich, I. Mukhametzhanov, P. Chen, and A. Madhukar, J. Appl. Phys. **84**, 3342 (1998).
[24] C. Lobo, R. Leon, S. Marcinkevicius, W. Yang, P. C. Sercel, X. Z. Liao, J. Zou, and D. J. H. Cockayne, Phys. Rev. B **60**, 16 647 (1999).
[25] R. Notzel, J. Temmyo, H. Kamada, T. Furuta, and T. Tamamura, Appl. Phys. Lett. **65**, 457 (1994).
[26] A. J. Nozik and O. I. Micic, MRS Bull. **23**, 24 (1998).
[27] D. G. Deppe and Q. Deng, Appl. Phys. Lett. **73**, 3536 (1998).
[28] B. Ohnesorge, M. Albrecht, J. Oshinowo, A. Forchel, and Y. Arakawa, Phys. Rev. B **54**, 11 532 (1996).
[29] D. Morris, N. Perret, and S. Fafard, Appl. Phys. Lett. **75**, 3593 (1999).
[30] R. Ferreira and G. Bastard, Appl. Phys. Lett. **74**, 2818 (1999).
[31] P. N. Brounkov, A. Polimeni, S. T. Stoddart, M. Henini, L. Eaves, P. C. Main, A. R. Kovsh, Y. G. Musikhin, and S. G. Konnikov, Appl. Phys. Lett. **73**, 1092 (1998).