State mixing in InAs/GaAs quantum dots at the pressure-induced Γ-X crossing

G.H. Li,* A.R. Goñi, K. Syassen, O. Brandt,† and K. Ploog†
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany
(Received 15 July 1994)

We have measured low-temperature ($T = 10$ K) photoluminescence spectra of InAs quantum dots embedded in a GaAs crystalline matrix under hydrostatic pressures up to 7 GPa. Below 4.2 GPa the spectra are dominated by the emission related to the Γ-like electron–heavy-hole exciton in the InAs dots. Above 4.2 GPa the spectra show two luminescence bands that shift to lower energies with increasing pressure. These bands are attributed to the type-I transition between X_{xy} and heavy-hole states in the dots and the type-II transition from X states in GaAs to InAs heavy-hole states, respectively. In the Γ-X crossover regime we find evidence for a pronounced anticrossing behavior due to mixing between InAs Γ-like and GaAs X-like states. The corresponding interaction potential is estimated to be 9 meV, which is an order of magnitude larger compared to mixing interactions reported for semiconductor superlattices.

I. INTRODUCTION

Electron states and optical properties of low-dimensional semiconductor systems like quantum wires and quantum dots[1–4] have become increasingly important recently. Developments in molecular-beam epitaxy (MBE) technology offer to fabricate these structures in a well-controlled way. Using a slightly misoriented GaAs substrate, it is possible to grow InAs quantum dots in a crystalline GaAs matrix due to the aggregation of the deposited InAs on the terraced surface.[3,4] Spectroscopic investigations of these InAs quantum dot samples have revealed optical properties which differ drastically from those of simultaneously grown InAs monolayer samples. In particular, the dot samples exhibit an inhibited relaxation of excitons to the ground state and longer excitonic lifetimes.[3,5] These results confirm the zero-dimensional properties of the InAs dot structures.

The conduction band Γ and X_z states (here z stands for the growth direction) in a spatially confined system mix with each other due to the potential step at the interface.[6,7] This leads to an anticrossing-type behavior of these states, if the energy separation of the uncoupled states is less than the interaction strength. Meynadier *et al.*[8] have observed this type of anticrossing in a GaAs/AlAs short period superlattice near an *electric-field-induced* Γ-X crossover. Several detailed studies of the *pressure-induced* Γ-X crossover in the GaAs/AlAs layer systems have been reported (see, e.g. Refs. 9–11), but no evidence of a Γ-X anticrossing behavior has been observed. This is probably due to the small interaction potential [about 1 meV (Ref. 8)] in these systems. In quantum dots, however, the movement of carriers is restricted in all three directions in space and the mixing of states is expected to be more pronounced. Therefore, quantum dot samples are more suitable for the investigation of mixing effects near a Γ-X degeneracy.

Here, we report low-temperature photoluminescence (PL) spectra of a sample consisting of InAs dots in a GaAs matrix under hydrostatic pressures up to 7 GPa. From the pressure dependence of the PL emission energies, we obtain clear evidence for an anticrossing behavior near the Γ-X conduction band crossover in the quantum dots. We find a quite strong interaction potential of 9 meV which is much larger than that in a reference InAs monolayer sample (3 meV). We attribute this difference in the coupling constant to the enhanced mixing effect arising from the breaking of translational symmetry by the dot potential along all three perpendicular directions. This is, to our knowledge, the first observation for an anticrossing behavior near a *pressure-driven* Γ-X crossover.

II. EXPERIMENTAL DETAILS

The InAs dots are grown by conventional MBE on semi-insulating GaAs substrates, misoriented by 3.2° with respect to the [100] direction. A reference InAs monolayer (ML) sample with [100]-oriented substrate is simultaneously grown side by side. Both samples consist of 10 InAs sub-ML separated by about 100 ML of GaAs. The InAs dots are formed due to the aggregation of deposited InAs at the step edges provided by the specific terrace configuration, which is induced by the surface tilt with respect to [100]. Details of the growth procedure have been given elsewhere.[3] The average InAs layer thickness is 0.8 ML for the monolayer sample and 0.3 ML for the dot sample, as determined by high-resolution double-crystal x-ray diffraction. The lateral extent of the dots is limited by the mean terrace size of 7 nm as determined by the misorientation angle.

The samples were mechanically thinned to total thicknesses of about 20 μm, and then cut into pieces of about 100×100 μm^2 in size. High pressure photoluminescence and optical absorption measurements were performed at $T = 10$ K using a diamond-anvil cell in combination with a helium-flow cryostat. Condensed helium was used as the pressure-transmitting medium. Pressure was always

changed at 300 K in order to ensure the best possible hydrostatic conditions at low temperatures. Pressure was measured *in situ* using the ruby luminescence method[12] and the temperature correction of the pressure calibration according to Ref. 13. The luminescence was excited by the 514.5 nm line of an Ar^+ ion laser at a power density of about 20 W/cm^2. For absorption measurements white light from a tungsten lamp was focused onto the sample forming a spot of about 35 μm in diameter. Both the PL and the transmitted light were analyzed by a 0.6 m single-grating spectrometer equipped with a GaAs photomultiplier operating in fast photon-counting mode. The absorption spectra were corrected for the spectral dependences of the various optical components.

III. RESULTS AND DISCUSSION

Figure 1 shows zero-pressure PL spectra of the dot sample (solid line) and the reference monolayer sample (dashed line) measured at 10 K. The dominant peaks in the PL spectra (labeled as D for the dot sample and M for the ML sample) are attributed to the radiative recombination of the heavy-hole exciton in the InAs monolayers or dots. The energy position of peak D is somewhat higher than that of peak M and its linewidth (full width at half maximum), 16 meV, is about two times larger than that of peak M (7.5 meV). The broadening of the PL emission line in the case of the dot samples is discussed in detail in Refs. 3 and 5. The two higher energy lines in Fig. 1 at 1.516 eV (FE) and 1.495 eV (C) are related to the free exciton and the band-to-carbon-acceptor recombination in GaAs, respectively.

With increasing pressure the PL peaks shift to higher energy, as demonstrated by the spectra for the dot sample shown in Fig. 2(a). The spectra for the monolayer sample show a similar pressure dependence. At about 4.0 GPa, an additional very weak PL peak (X) related to the X excitons in GaAs appears (hardly seen on the scale of the spectra in Fig. 2), indicating the Γ-X crossover in the GaAs matrix. Above 4.2 GPa the intensity of peak D decreases dramatically. Furthermore, above 4.2 GPa, two new bands (D_1, D_2) appear below the GaAs X-related peak [see Fig. 2(b)], which shift to lower energy with increasing pressure at a rate which is slightly larger than that of the X peak.

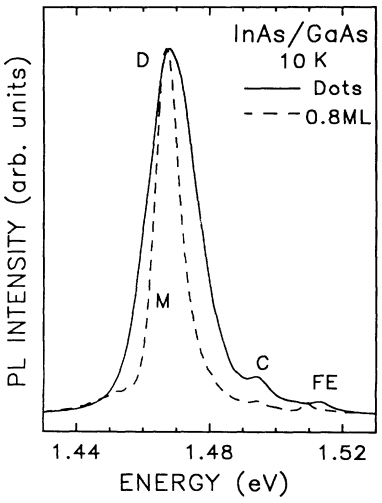

FIG. 1. Photoluminescence spectra of InAs dots (solid line) and InAs monolayers (dashed line) in a GaAs matrix at zero pressure and 10 K. The spectra have been normalized.

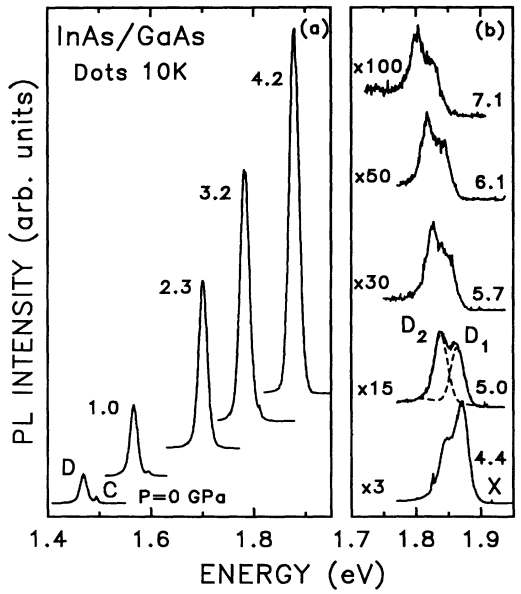

FIG. 2. Photoluminescence spectra at different pressures for InAs dots in a GaAs matrix for (a) $P \leq 4.2$ GPa and (b) $P > 4.2$ GPa. The dashed curves in the spectrum at 5.0 GPa represent fitted Gaussian line profiles.

The pressure dependences of the PL peak energies are plotted in Fig. 3. The energy position of the free exciton in GaAs (FE) is obtained from the absorption edge of GaAs measured in transmission. Since the PL peaks D_1 and D_2 overlap, their energy positions, linewidths and peak intensities are determined from a least-squares fit of Gaussian line profiles, as indicated for the spectrum at 5.0 GPa in Fig. 2(b). The solid lines in Fig. 3 represent the results of least-squares fits to the experimental PL peak energies using first or second-order polynomials. The corresponding parameters are given in Table I.

The inset of Fig. 3 shows the variation of the peak intensities for lines D and D_1 with pressure. The intensity of peak D increases with pressure in the range from 0 to 4.2 GPa. This effect is in part attributed to an increase in the number of carriers captured in the InAs dots as pressure shifts the band gap closer to the laser excitation energy. The intensity of peak D_2 is nearly the same as that of peak D_1, except at pressures near the crossover point where D_2 is significantly weaker than D_1.

The spectra of the monolayer sample also show, at pressures above 4.2 GPa, two X-related bands with similar characteristics concerning the pressure dependence of their peak energies and peak intensities. As we have previously demonstrated,[14] these two bands in the InAs monolayer sample (labeled as M_1 and M_2) correspond to the type-II transition from the X valley in GaAs to the heavy-hole state in the InAs monolayer and the type-I

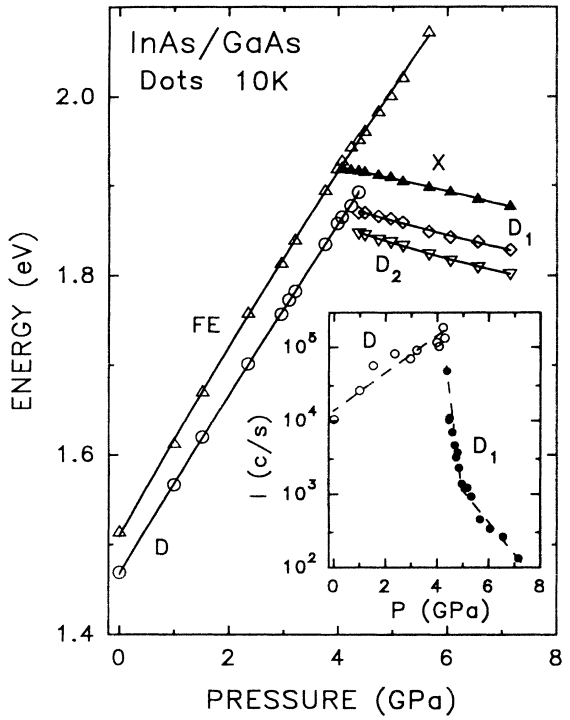

FIG. 3. Pressure dependence of photoluminescence peak energies of the InAs/GaAs dot sample. Energies D, D_1, and D_2 refer to emission bands related to the InAs dots (see text for the assignment), and FE and X refer to the free exciton and X-related emission in GaAs, respectively. Data for the free exciton in GaAs were obtained from absorption measurements. The solid lines represent least-squares fits to the data. The inset shows the pressure dependence of the peak intensity of peaks D and D_1.

transition within the InAs monolayer from the X_{xy} conduction band states to the heavy-hole state, respectively. In view of these similarities, we attribute the peaks D_1 and D_2 of the InAs dot sample to the same optical transitions.

After having presented the gross features of the pressure-induced changes of the electronic structure of the InAs dot sample, we now turn to the discussion of state mixing effects near the Γ-X crossover. Representative PL spectra of the dot and monolayer samples in a narrow pressure range around 4.2 GPa are shown in Fig. 4. The bottom and top spectra represent the situation just below and above the Γ-X crossover, respectively. The middle spectra correspond to the crossover points where all Γ- and X-related PL peaks can be observed.

TABLE I. Energies and pressure coefficients of PL peaks in a InAs/GaAs quantum dot sample as obtained from fitting a quadratic relation $E(P) = E(P=0) + a_1 \times P + a_2 \times P^2$ to experimental data.

Peak	$E(0)$ (eV)	a_1 (meV/GPa)	a_2 (meV/GPa^2)
D	1.468(2)	102(2)	-1.3(5)
FE	1.510(2)	109(2)	-1.8(5)
D_1	1.939(5)	-16(1)	
D_2	1.919(5)	-17(1)	
X	1.978(2)	-14(1)	

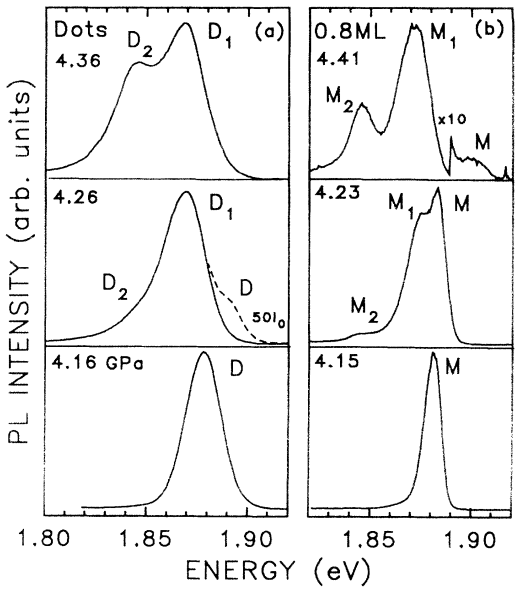

FIG. 4. Photoluminescence spectra of (a) the InAs dot sample and (b) the InAs monolayer sample in the pressure range near the Γ-X crossover (see text for peak assignments). The spectra have been normalized. Spectra were measured using an excitation power density of $I_0 = 20\ W/cm^2$, except for the part represented by a dashed curve.

In Fig. 5, we summarize the results obtained in the range near the Γ-X crossover for the PL peak energies of the dot (full symbols) and ML sample (open symbols) as a function of pressure. The intensities of peaks D and M decrease dramatically after the crossover, such that

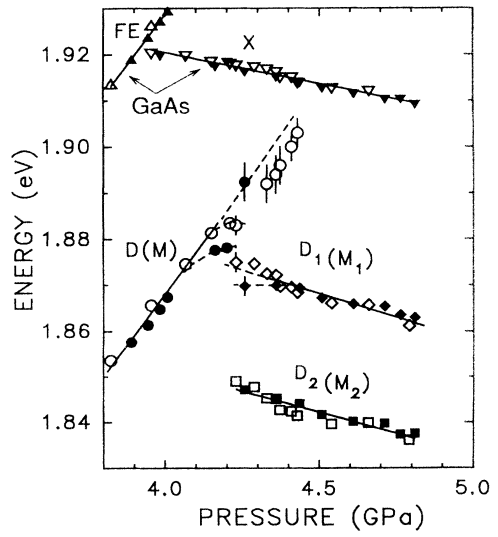

FIG. 5. Pressure dependence of photoluminescence peak energies in the pressure range near the Γ-X crossover. The full and open symbols represent the data of the dot and monolayer samples, respectively. The solid lines represent results of least-squares fits (see text for details).

the energy position at higher pressures is obtained with relatively large error. The solid lines in Fig. 5 represent fits to the data using a linear energy versus pressure relation. To obtain the fitted lines, only data well below and above the crossover point were used for peaks D (M) and D_1 (M_1), respectively. It is obvious from Fig. 5 that near the crossover the energies of peaks D (M) and D_1 (M_1) deviate significantly from the extrapolated linear pressure dependences. This effect is more pronounced for the dot sample. The deviation from a linear behavior points to an anticrossing behavior of the energies of peaks D (M) and D_1 (M_1), which is a manifestation of mixing effects among conduction band states. In addition, the dot as well as monolayer sample show a peculiar jump between energies of the $D(M)$ and D_1 (M_1) peaks just at the crossover point near 4.2 GPa. We show below that this jump rises from the difference in exciton binding energies of Γ- and X-related states.

As mentioned above an interaction or mixing between the Γ and X_z conduction band states is expected to occur in semiconductor heterostructures due to the potential step at the interfaces.[6] In first-order perturbation theory the energy position of two interacting states can be expressed as[7]

$$E_{\pm} = \frac{1}{2}\{(E_\Gamma + E_X) \pm [(E_\Gamma - E_X)^2 + 4V^2]^{1/2}\} , \tag{1}$$

where E_Γ and E_X are the energies of the Γ and X_z states without interaction, and V is the interaction potential. If we write for the pressure dependence of E_Γ and E_X

$$E_\Gamma = E(P_c) + a_\Gamma(P - P_c) , \tag{2}$$
$$E_X = E(P_c) + a_X(P - P_c) , \tag{3}$$

the pressure dependence of $E_\pm$ will be

$$E_\pm(P) = E(P_c) + \tfrac{1}{2}(a_\Gamma + a_X)(P - P_c) \pm\{[\tfrac{1}{2}(a_\Gamma - a_X)(P - P_c)]^2 + V^2\}^{1/2} , \tag{4}$$

where P_c and $E(P_c)$ are pressure and energy $[E_\Gamma(P_c) = E_X(P_c)]$ at the crossover point, a_Γ and a_X are the pressure coefficients of E_Γ and E_X, respectively. Since the observed PL peaks correspond to the recombination of excitons, the PL peak position is

$$E_{\rm PL}(P) = E_-(P) - R(P), \tag{5}$$

where R is the exciton binding energy. Taking into account an anisotropy of effective masses, the binding energy is given by[15]

$$R = \frac{e^4\mu_\perp}{2\hbar\epsilon^2}z^2 , \tag{6}$$

with

$$z = \begin{cases} \frac{1}{\sqrt{|\alpha|}}\text{arcsh}(\sqrt{|\alpha|}) , & \alpha < 0 \\ 1 , & \alpha = 0 \\ \frac{1}{\sqrt{\alpha}}\arcsin(\sqrt{\alpha}) , & \alpha > 0 . \end{cases} \tag{7}$$

Here, $\alpha = 1 - \mu_\perp/\mu_\parallel$ is the anisotropy parameter, $\mu_\perp$ and $\mu_\parallel$ are the reduced effective masses perpendicular and parallel to the z axis, respectively. For the Γ states, we assume that $\mu_\perp^{-1} = \mu_\parallel^{-1} = m_e^{-1} + m_{hh}^{-1}$. For the X_z states, $\mu_\perp$ and $\mu_\parallel$ are the longitudinal and transverse reduced effective masses of excitons formed by an electron at the X valleys and a heavy hole at Γ. The effect of the state mixing is taken into account in the calculation of the binding energy by using an approximate expression,

$$\mu_\parallel = A_\Gamma\mu_\parallel(\Gamma) + A_X\mu_\parallel(X) , \tag{8}$$

where

$$A_\Gamma = \frac{V^2}{(E_\Gamma - E_\pm)^2 + V^2} ,$$
$$A_X = 1 - A_\Gamma ,$$

are the squared coefficients of Γ and X_z state wave functions forming the mixed states. Equation (8) implies that a mixing takes place only between the z component of the wave functions.

Calculated energies E_- and $E_{\rm PL}$ are presented in Fig. 6 together with the experimental energies of peaks $D(M)$ and $D_1(M_1)$. The solid and dot-dashed curves correspond to the dot and monolayer sample, respectively. The parameters used in the calculation, which are the same for both samples with the exception of the interaction potential V, are listed in Table II. The values for P_c, gap energies at P_c, and interaction potential were obtained from a least-squares fit. The agreement between experimental data and calculated results is within experimental uncertainty.

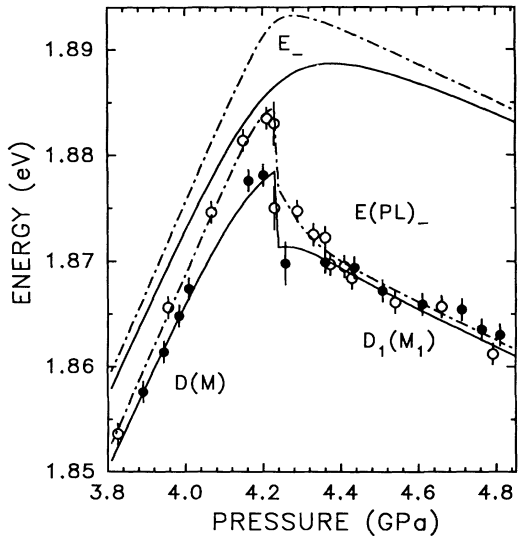

FIG. 6. Calculated results for the anticrossing behavior of the Γ and X_z states. The solid and dot-dashed curves refer to the dot and monolayer sample, respectively. The two upper curves represent the results [Eq. (4)] for the E branch of the Γ-X coupled states. The curves through the data points for PL peaks D(M) and $D_1(M_1)$ are obtained if the change of the exciton binding energy at the crossover pressure is taken into account.

TABLE II. Parameters entering the calculation of the pressure-induced Γ-X anticrossing behavior of PL peaks in InAs/GaAs dot and monolayer samples: electron effective masses at the Γ and X point, heavy-hole effective mass, linear pressure coefficients of the Γ and X conduction band minima near the crossover, crossover pressure and energy, and the interaction potentials. The effective masses are taken from Ref. 16.

Parameter	Value
m_e^Γ	0.067
$m_{e\perp}^X$	0.23
$m_{e\parallel}^X$	1.3
m_{hh}^Γ	0.48
a_Γ	0.085 eV/GPa
a_X	-0.018 eV/GPa
P_c	4.23±0.05 GPa
$E_\Gamma(P_c) = E_X(P_c)$	1.896±0.005 eV
V(monolayer)	3±1 meV
V(dots)	9±1 meV

In the calculation, the state mixing is revealed by the anticrossing behavior of the emission peaks, i.e., the departure of E_{PL} from a linear pressure dependence while approaching P_c from below and above. The observed jump in the energy E_{PL} at the crossover pressure originates from the large difference in binding energy between the Γ and X excitons. The Γ-X state mixing due to the potential step at the InAs/GaAs interfaces involves mainly the component of the electron wave function which depends on the z coordinate. As a consequence, the excitonic properties change abruptly at the crossover, resulting in a discontinuity of the pressure dependence of the PL peak energy.

The interaction potential for the monolayer (3±1 meV) is comparable in magnitude to the result of Meynadier *et al.*[8] They obtained an interaction potential of 1 meV for a GaAs(35 Å)/AlAs(80 Å) superlattices from the electric-field-induced Γ-X anticrossing. On the other hand, the interaction potential for the quantum dots (9±1 meV) is significantly larger than that of the monolayers. This is direct experimental evidence that the mixing between Γ and X_z states is enhanced by the potential step at the edges of the dot, which cause the breaking of translational invariance also in the plane perpendicular to the z direction.

In summary, we have investigated the low-temperature photoluminescence of a sample with InAs dots in a GaAs matrix at high pressures. At pressures below 4.2 GPa the dominant peak in the PL spectra (D) corresponds to the radiative recombination of the excitons formed from electron and heavy hole states at Γ. Above 4.2 GPa, this peak vanishes and two new emission bands (D_1 and D_2) appear, which are attributed to the type-II transition from X states in GaAs to the heavy-hole states in InAs and the type-I transition within InAs involving the X_{xy} and heavy-hole states, respectively. Thus, the Γ-X crossover occurs at about 4.2 GPa in the InAs dots which is close to the direct-indirect transition in GaAs. Near the Γ-X crossover, the pressure dependence of the energies of peaks D and D_1 show a significant deviation from a linear behavior, indicating an anticrossing behavior. This effect is attributed to a relatively strong interaction between the InAs Γ-like state and GaAs X-like state in the case of quantum dots. A reference InAs/GaAs monolayer sample is also measured. The spectral character is similar to that of the dots except at the Γ-X crossover point, where the emission lines of the monolayer sample show a less pronounced nonlinear pressure dependence. A perturbation theory expression has been used to simulate the anticrossing behavior at the Γ-X crossover point. The interaction potential of Γ and X_z states is then estimated to be 9 and 3 meV for dot and monolayer samples, respectively.

ACKNOWLEDGMENTS

We thank W. Dieterich, U. Oelke, and U. Engelhardt for expert technical assistance. G. H. L. gratefully acknowledges financial support from the Max-Planck-Gesellschaft.

*Permanent address: Institute of Semiconductors, Chinese Academy of Science, Beijing, China.
†Present address: Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany.

[1] D. Heitmann, T. Demel, P. Grambow, M. Kohl, and K. Ploog, in *Proceedings of the 20th International Conference on the Physics of Semiconductors, Greece, 1990*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 13.
[2] K. Kash, J. Lumin. **46**, 69 (1990).
[3] O. Brandt, L. Tapfer, K. Ploog, R. Bierwolf, M. Hohenstein, F. Phillipp, H. Lage, and A. Heberle, Phys. Rev. B **44**, 8043 (1991).
[4] K. Ploog and O. Brandt, Semicond. Sci. Technol. **8**, S229 (1993).
[5] O. Brandt, G. C. La Rocca, A. Heberle, A. Ruiz, and K. Ploog, Phys. Rev. B **45**, 3803 (1992).
[6] L. J. Sham, and Y. T. Lu, J. Lumin. **44**, 207 (1989).
[7] M. A. Gell, D. Ninno, M. Jaros, D. J. Wolford, T. F. Keuch, and J. A. Brandley, Phys. Rev. B **35**, 1196 (1987).
[8] M.-H. Meynadier, R. E. Nahory, J. M. Worlock, M. C. Tamargo, J. L. de Miguel, and M. D. Sturge, Phys. Rev. Lett. **60**, 1338 (1988).
[9] D. J. Wolford, T. F. Kuech, J. A. Brandley, M. A. Gell, D. Ninno, and M. Jaros, J. Vac. Sci. Technol. B **4**, 1043 (1986).
[10] G. H. Li, D. S. Jiang, H. X. Han, Z. P. Wang, and K. Ploog, Phys. Rev. B **40**, 10 430 (1989).
[11] M. Holtz, R. Cingolani, K. Reimann, R. Muralidharm, K. Syassen, and K. Ploog, Phys. Rev. B **41**, 3641 (1990).
[12] G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973

(1975); H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[13]R. A. Noack and W. B. Holzapfel, in *High Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 748; D. M. Adams, R. Appleby, and S. K. Sharma, J. Phys. E **9**, 1140 (1976); I. F. Silvera and R. J. Wijngarden, Rev. Sci. Instrum. **56**, 121 (1985).

[14]G. H. Li, A. R. Goñi, C. Abraham, K. Syassen, P.V. Santos, A. Cantarero, O. Brandt, and K. Ploog, Phys. Rev. B **50**, 1575 (1994).

[15]B. Gerlach and J. Pollmann, Phys. Status Solidi B **67**, 93 (1975); A. R. Goñi, A. Cantarero, U. Schwarz, K. Syassen, and A. Chevy, Phys. Rev. B **45**, 4221 (1992).

[16]*Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, H. Weis, and M. Schulz, Landolt-Börnstein, New Series, Vol. 17, Pt. a (Springer, Heidelberg, 1982).