Electronic subband structure of $InP/In_xGa_{1-x}P$ quantum islands from high-pressure photoluminescence and photoreflectance

C. Ulrich, S. Ves,* A.R. Goñi, A. Kurtenbach, K. Syassen, and K. Eberl
Max-Planck-Institut für Festkörperforschung , Heisenbergstrasse 1, 70569 Stuttgart, Germany
(Received 21 June 1995)

We have measured low-temperature photoluminescence (PL) under hydrostatic pressure and photomodulated reflectivity (PR) at ambient conditions of nanoscale InP islands embedded in an $In_{0.48}Ga_{0.52}P$ matrix-grown lattice matched on a GaAs substrate. The pressure experiments cover the range of the pressure-induced Γ-X conduction-band crossover both in the InP islands and in the $In_xGa_{1-x}P$ barrier. Below the Γ-X crossings the PL emission is dominated by direct optical transitions in the islands and in the barrier, both shifting to higher energy with increasing pressure. The PL bands observed above the crossover are broad and weak, and their pressure dependence turns to negative. These bands are therefore attributed to the indirect optical transitions between X conduction-band states and the Γ heavy holes of the InP islands and the $In_xGa_{1-x}P$ matrix, respectively. PR spectra show two well-resolved features below the direct gap of $In_xGa_{1-x}P$, which are assigned to optical transitions between heavy-hole subbands and electron levels of the InP islands. From the combined PL and PR data we derive a value of 80 ± 15 meV for the valence-band offset in the strained $InP/In_xGa_{1-x}P$ system. The interpretation of experimental results in terms of subband-structure calculations within the envelope-function approximation allows us to estimate the amount of strain relaxation in the islands.

I. INTRODUCTION

In recent years low-dimensional semiconductor structures such as quantum wires and dots have attracted attention due to their striking quantum mechanical properties and their potential for device applications. Usually the level of perfection of such nanostructures is limited by the lithographic processing. This problem is circumvented with the developments on the growth of self-assembling quantum dots structures.[1] One approach consists of the epitaxial growth of materials with a large lattice mismatch, for which the transition from two- to three-dimensional growth is induced by the built-in misfit strain.[2] In this way, InP islands of very small lateral size (20 – 50 nm) have been grown in an $In_{0.48}Ga_{0.52}P$ matrix which is lattice matched to a GaAs substrate.[3–6]

$InP/In_xGa_{1-x}P$-island samples with different island densities and sizes have been prepared by molecular beam epitaxy (MBE) (Ref. 6) or metalorganic chemical vapor deposition (MOCVD).[3–5] The island morphology has been verified primarily by atomic force microscope (AFM) images taken before overgrowth of the cap layer. Recently, transmission electron microscopy (TEM) has also been used for structural characterization.[7] Evidence for island formation has been also obtained from the typical blueshift of the photoluminescence (PL) emission with respect to the direct band gap E_0 of InP.[3,6] The zero-dimensional (0D) character of the quantum confined states has been established through time-resolved studies of the dependence of the PL decay times on excitation power and temperature.[7] Nevertheless, very basic information about the band alignments in the strained $InP/In_xGa_{1-x}P$ system and a clear picture for the stress effects is still lacking.

For another class of 0D self-assembled structures based on the InAs/GaAs material system, high-pressure studies of the low-temperature luminescence have been demonstrated to be a powerful method for gaining insight into the electronic subband structure.[8,9] Key information is obtained by tuning the energy levels through the Γ-X degenerancies of conduction-band states. With increasing pressure it is also possible to induce in $In_xGa_{1-x}P$ a transition from a direct to an indirect band-gap material due to the very different dependence on pressure of the conduction-band minima at the Γ and X points of the Brillouin zone.[10,11] The valence-band offset can be directly obtained from the PL data for pressures above the Γ-X crossover provided the type-I and type-II indirect emission within the barrier and between barrier and dot, respectively, are simultaneously observed.[8,9,12,13]

In this work we report the dependence on pressure of the low-temperature photoluminescence measured in two $InP/In_xGa_{1-x}P$ quantum island samples with different average island sizes. In both cases pressure was raised above the Γ-X crossover pressure for the InP islands and the $In_xGa_{1-x}P$ barrier as well. In spite of the large bandwidth ($\approx$ 50 meV) of the PL emission in the indirect case, these data allow us to obtain an estimate for the band offsets in the strained $InP/In_xGa_{1-x}P$ system. In addition, we have measured optical transition energies between excited electron and hole states of the InP islands by means of photoreflectance spectroscopy at ambient temperature and pressure conditions. From the interpretation of these results in terms of effective-mass subband-structure calculations and by accounting for the effect of built-in stress within $\mathbf{k}\cdot\mathbf{p}$ theory we are able to separate the effects of confinement and strain for samples with different island density and size.

0163-1829/95/52(16)/12212(6)/$06.00

II. EXPERIMENTAL DETAILS

The samples were grown on (001) GaAs substrates by solid-source MBE. The deposition sequence consists of a GaAs buffer layer followed by 200 nm of $In_{0.48}Ga_{0.52}P$ and 3–10 monolayers (ML) of InP at a previously calibrated rate of 0.485 ML/s. Finally, another 200-nm-thick $In_{0.48}Ga_{0.52}P$ cap layer is overgrown on top of the InP islands. Further details of the growth procedure are given elsewhere.[6,7] The AFM pictures show that for a sample of nominally 3 ML of InP the islands form, depending on the growth conditions, with a density of $(3\pm2)\times10^{10}$ cm^{-2} having a diameter of about 20–30 nm and a height of 5–10 nm. There is no further increase in density for a 7 ML sample but the island diameter increases up to 40–50 nm.[7]

For the pressure experiments the samples were mechanically thinned to a total thickness of about 30 μm and then cut into pieces of about 100×100 μm^2 in size. High-pressure PL measurements were carried out at 9 K utilizing a diamond-anvil cell in combination with a helium-flow cryostat. Condensed helium was used as a pressure transmitting medium. The pressure was measured *in situ* using the ruby luminescence method[14] with temperature correction of the pressure calibration.[15] The luminescence was excited by the 488 nm line of an Ar^+ ion laser at a power of 6 mW in front of the cryostat. The emitted light was analyzed by a 0.6 m single-grating spectrometer equipped with a GaAs photomultiplier operating in fast-photon-counting mode. For photomodulated reflectivity measurements a monochromatic probe beam was obtained by passing the light of a tungsten-halogen lamp through a 1/4 m Jarrell-Ash monochromator. The modulation was carried out by focusing the blue light of a He-Cd laser (441.6 nm) together with the probe beam onto the same spot on the sample. The reflected intensity was then measured with a Si-*PIN* diode and detected using a double lock-in technique, in which the probe and laser beams are chopped at different frequencies with detection occurring at the sum frequency. In this way strong background signals from sample luminescence and scattered light of the laser were largely suppressed. Further details of the PR setup will be given elsewhere.[16]

III. RESULTS AND DISCUSSION

Figure 1 shows the PL and PR spectra measured at ambient pressure for two samples of 3 ML and 7 ML nominal InP growth thickness. The dominant peak (D) in the low-temperature PL spectra corresponds to radiative recombination between the lowest electron and heavy-hole ($11H$) states of the InP islands. This peak appears at lower energy than the Γ emission of the $In_xGa_{1-x}P$ barrier[17] and exhibits a strong blueshift with respect to the band-gap energy of bulk InP [$E_0 = 1.41$ eV at 10 K (Ref. 10)]. The blueshift, which is larger for the 3 ML sample, arises from the combined effects of confinement and strain in the InP islands. The width of peak D is approximately 25 meV for both samples. It is mainly determined by the size distribution of the islands.[7]

Photoreflectance spectra show several features which correspond to the peaks in emission (the energy shifts between related PL and PR features in Fig. 1 are due to the different temperature of the measurements). An additional optical transition labeled as $22H$ is clearly observed in the PR spectra of the 7 ML sample. Typically, the oscillator strength of the optical interband transitions in PR spectra of quantum wells is about five times larger for heavy holes than for light holes.[16,18] Hence, this additional structure in PR is attributed to optical transitions between confined heavy-hole and electron ($22H$) states of the InP islands with subband index $n = 2$. For the 3 ML sample the $11H$ feature of the InP islands is partly masked by the PR signal of the GaAs $E_0+\Delta_0$ transition (Δ_0 is the spin-orbit splitting of the valence band at the Γ point). The arrows in Fig. 1(b) indicate the energy position of the observed optical transitions as obtained from lineshape fits to the PR data using the fitting function of Ref. 19.

Luminescence spectra of the 3 ML sample measured at 10 K and at different pressures are shown in Fig. 2. For pressures below 2.8 GPa all the observed features in the PL shift to higher energies with increasing pressure. At this pressure (P_c) the Γ-X conduction-band crossover takes place in the $In_xGa_{1-x}P$ barrier, as is revealed by the negative pressure dependence and broadening of the

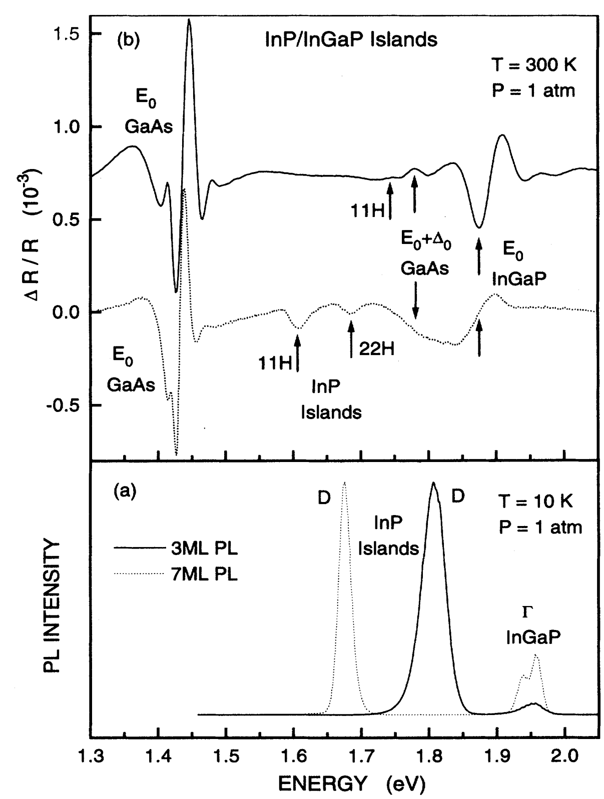

FIG. 1. (a) Ambient pressure photoluminescence spectra at 10 K and (b) photoreflectance spectra at 300 K of $InP/In_xGa_{1-x}P$ island samples grown with 3 ML (solid lines) and 7 ML (dotted lines) nominal thickness.

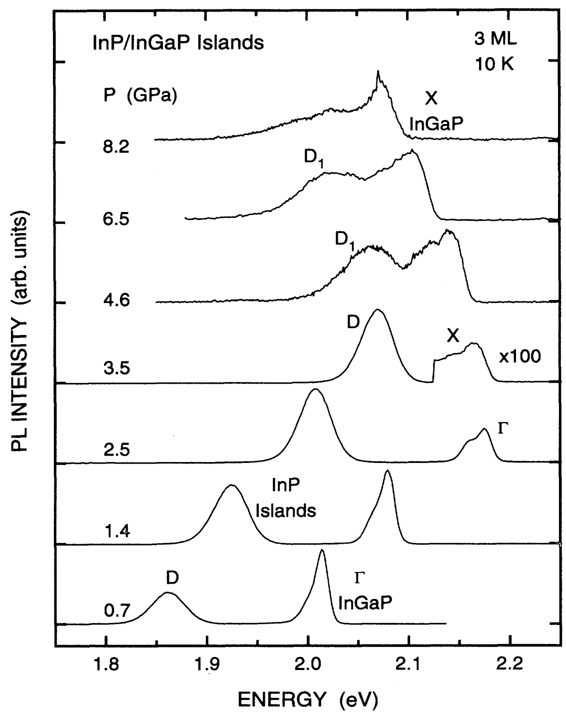

FIG. 2. PL spectra of the 3 ML InP island sample for different pressures. Each spectrum has been normalized to the maximum intensity, except for the part of the 3.5 GPa spectrum.

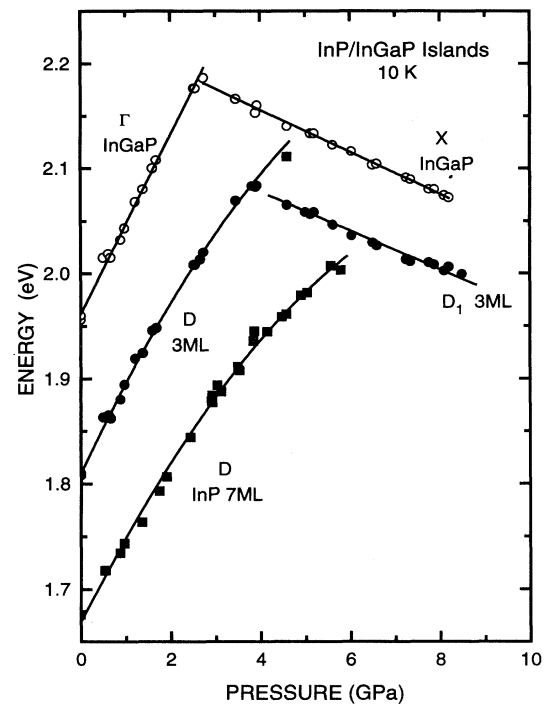

FIG. 3. Pressure dependence of the energy of PL peaks for the 3 ML and 7 ML InP island samples.

barrier PL peak (X). Above P_c the PL intensity of the direct transitions decreases by three orders of magnitude in a very narrow pressure range of 0.5 GPa. This crossing occurs somewhat later for the InP islands, at about 3.8 GPa. The PL band D_1 corresponds to the indirect emission from the X conduction states of the islands.

A similar behavior of the luminescence is observed for the 7 ML sample below the Γ-X crossover. In the indirect case, however, the PL emission of the 7 ML InP islands was no longer observable, but instead a weak indirect luminescence of the GaAs buffer layer appeared. It is shown below that this behavior results from subtle changes in the alignment of the X conduction-band edges in the islands and the barrier of the two samples with different nominal InP thickness.

In Fig. 3 we summarize the results for the pressure dependence of the PL peak energies for the samples of 3 ML and 7 ML thickness. The solid lines represent the results of least-squares fits to the experimental data using quadratic or linear relations. The corresponding first- and second-order pressure coefficients are listed in Table I. Within experimental uncertainty these coefficients agree well with those measured for bulk InP and the $In_{0.5}Ga_{0.5}P$ alloy.[10,11,13,20,21]

Important information about the band offsets (ΔV_c, ΔV_v) for the strained InP/$In_xGa_{1-x}P$ system can be obtained from the PL data in the indirect gap case. We have schematically illustrated in Fig. 4 the proposed band profile for the two different samples studied in PL. Peaks X and D_1, observed for pressures above the crossover, are attributed to the type-I indirect optical transitions from the conduction-band X point to the heavy holes at Γ in the $In_xGa_{1-x}P$ barrier and in the InP islands, respectively. In contrast to the observations made for a similar InAs/GaAs quantum dot system,[9] the type-II transition from the $In_xGa_{1-x}P$ X valleys to the heavy holes in InP, which is indirect in real and **k** space, is missing in PL. Either its intensity is too weak due to the effect of the rough island interfaces or it cannot be resolved because of the relatively large widths of the indirect emission bands (see Fig. 2). The temperature dependence of the D_1 peak in the 3 ML sample exhibits a thermally activated behavior, being quenched at about 100 K. This suggests that the X minimum in the islands is approximately 10 meV below that of the $In_xGa_{1-x}P$ matrix. In this way, from the energy difference between peaks X and D_1 (see Table II) and by taking into account the confinement energy of the heavy holes in the InP islands ($\sim$10 meV) we obtain the value of ΔV_v=80$\pm$15 meV for the valence-band offset of the strained InP/$In_xGa_{1-x}P$ heterointerface.

An interesting result is the fact that line D_1 is completely absent in the PL spectra of the 7 ML sample. This leads to the conclusion that in going from 3 to 7 ML of InP a reversal of the position of the absolute X conduction-band minimum of the InP/$In_xGa_{1-x}P$ dot system has occurred. As indicated in Fig. 4, for the 3 ML sample the X minimum of the InP islands is lowest in energy, whereas for the 7 ML sample these states are placed above the energy E_X of the X point of the $In_xGa_{1-x}P$ barrier. In the latter case the photoexcited electrons would not be effectively captured in the islands,

TABLE I. Coefficients describing the dependence of the PL bands of the $InP/In_xGa_{1-x}P$ monolayer structure on pressure obtained from least-square fits to the experimental data using $E(P) = E(0) + a_1P + a_2P^2$.

Peak		$E(0)$ (eV)	a_1 (meV/GPa)	a_2 (meV/GPa^2)
3 ML dots	D	1.810(2)	91(2)	−5.0(5)
7 ML dots	D	1.668(2)	84(2)	−4.3(5)
$In_xGa_{1-x}P$ matrix	Γ	1.950(2)	83(2)	
3 ML dots	D_1	2.152(4)	−18.5(5)	
7 ML dots	D_1			
$In_xGa_{1-x}P$ matrix	X	2.238(4)	−19.5(5)	

the radiative recombination taking place mainly in the $In_xGa_{1-x}P$ matrix.

The reordering of the absolute X conduction-band minima is a consequence of a delicate balance between the effects of valence-band offset and strain. In ternary compounds of III-V semiconductors the energy of the conduction-band X point is mainly determined by the anion species; hence the X minima in bulk InP and $In_xGa_{1-x}P$ are roughly degenerate.[10,11] In the $InP/In_xGa_{1-x}P$ heterostructure the X point of InP is shifted in energy with respect to that of $In_xGa_{1-x}P$ by an amount given by the valence-band offset. On the other hand, the large built-in stress of the InP islands pushes the X minimum to lower energies by about 20 meV/GPa for hydrostatic compression.[21] Obviously, the energy shift due to predominantly isotropic stress is smaller for the 7 ML sample, for which a larger relaxation of the misfit strain is expected to occur during growth. We provide an estimation of such effects below.

Further insight into the electronic subband structure of the InP island system is gained by comparing the energies of the spectral features measured in PL and PR at ambient pressure with the results of effective-mass calculations of subband energies within the envelope-function approximation (EFA).[22] Here we simply assumed a square-well potential along only the growth direction (z hereafter) for describing the islands. This seems a good approximation because in quantum wells confinement effects go as the square of the well width and for the samples studied here the aspect ratio (height/diameter) of the islands ranges from 1:3 to 1:5 depending on nominal InP thickness. We also assume that the islands embedded in the $In_xGa_{1-x}P$ matrix are isotropically strained.[23] The energy separation between the confined well states is mainly determined by the *well width* (L_z^{eff}) and *potential depth* (ΔV_c, ΔV_v), while the strong blueshift of the island luminescence with respect to the E_0 gap of bulk InP is a consequence of the *compression* by the $In_xGa_{1-x}P$ matrix. We thus have adjusted these three parameters until a reasonable agreement between calculated and measured energies was obtained. The results of the calculations are listed in Table II together with the PL and PR data. The value of L_z^{eff}=5 nm for the effective well width of the 3 ML sample has been taken from AFM data.[7] The corresponding value for the 7 ML sample has been obtained by fitting to the experimental data. The conduction- and valence-band offsets of Table II have been calculated using the ratios of 70% and 30%, respectively, of the total band-gap discontinuity as in the case of $In_xGa_{1-x}P/Al_xIn_{1-x}GaP$ (Ref. 24) and the $In_xGa_{1-x}As/Al_xGa_{1-x}As$ system.[25]

We point out the good agreement of the calculated valence-band offset with the result derived from PL measurements in the pressure range above the Γ-X crossover. The energy difference ΔE_0 between the direct band-gap E_0 of the islands and of bulk InP (see Table II) is also obtained from fits to the measured energies within our simple model. Using the linear pressure coefficient for bulk InP of dE_0/dP = 84 meV/GPa,[26] ΔE_0 can be transformed into an effective hydrostatic pressure of 3.57(5) and 2.85(5) GPa for the 3 ML and 7 ML samples, respectively. These values, in turn, represent a compressive strain which is easily estimated using the literature data for the bulk modulus B_0 of InP.[26] For the 3 ML sample this strain amounts to 1.5%, whereas for the larger islands of the 7 ML sample it is slightly smaller (1.2%). These values are much smaller than the lattice mismatch of 3.7% between InP and $In_{0.48}Ga_{0.52}P$ indicating a significant relaxation of the built-in stress during the growth process.

Finally, we compare the results of the model calculations with PR measurements performed at ambient conditions for a series of six samples with nominal InP thick-

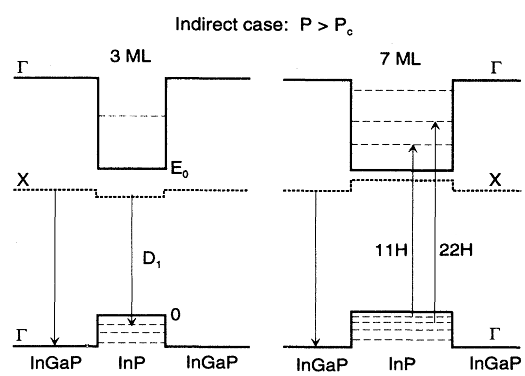

FIG. 4. Sketch of the Γ- and X-point conduction-band and Γ-point valence-band profile of the InP islands above the Γ-X crossover pressure. Arrows indicate the assignment of the observed optical transitions.

TABLE II. Measured and calculated energy differences (in meV) between optical transitions in the InP/$In_xGa_{1-x}P$ island system at ambient pressure (direct gap case) and above the crossover pressure (indirect gap case). $\Delta V_{c,v}$ are the band offsets.

Energy splitting	3 ML ($L_z^{\rm eff}$=5 nm) Experiment	Theory	7 ML ($L_z^{\rm eff}$=12 nm) Experiment	Theory
$E_0(In_xGa_{1-x}P)$–11H	PL: 140(5)	125	PL: 280(5)	235
	PR: 115(5)		PR: 260(5)	
22H–11H			PR: 75(5)	75
33H–11H				170
$X(In_xGa_{1-x}P)$–D_1	PL: 80(5)	55		45
$E_X^{\rm dot} - E_X(In_xGa_{1-x}P)$	PL: −10(5)	−5		30
$E_0^{\rm dot}$(InP)–$E_0^{\rm bulk}$(InP)		300		240
ΔV_c		140		180
ΔV_v	PL: 80(15)	60		80

nesses ranging from 3 to 10 ML. The energy position of the optical transitions obtained from line-shape fits to the PR spectra are plotted in Fig. 5 as a function of nominal InP thickness. The solid symbols correspond to the 11H and 22H transitions of the InP islands, whereas the open symbols indicate band-gap energies of the $In_xGa_{1-x}P$ barrier material and GaAs substrate. The solid curves in Fig. 5 represent the theoretical results of our model for the transition energies between confined states of the islands. For these calculations the values of the well width $L_z^{\rm eff}$ as well as the band-gap energy difference ΔE_0, i.e., the built-in stress, have been simply obtained from a linear interpolation using as reference the 3 and 7 ML samples. The description of the monolayer-thickness dependence of the transition energies within the model is quite good. We also notice that the model predicts the successive appearance with increasing InP thickness of transitions with higher subband index up to $n = 4$. These transitions are difficult to observe in the PR spectra due to interference with the strong signal of the $E_0+\Delta_0$ transition of the GaAs substrate.

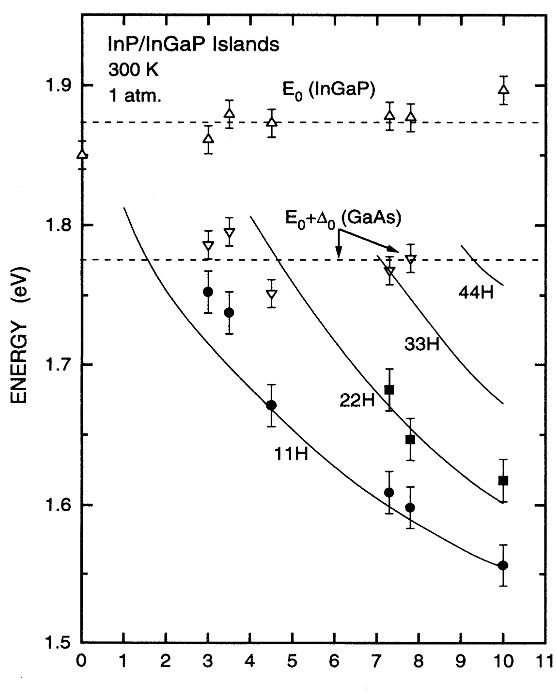

FIG. 5. Measured (symbols) and calculated (solid lines) energies for the optical transitions observed in PR spectra of samples with different nominal InP growth thickness of the islands.

In spite of the crude approximations our simple model provides a consistent picture of the electronic subband structure of the InP islands for the interpretation of the experimental evidence so far. More sophisticated models have to take into account the exact island morphology and also the strain distribution by employing finite-element methods.

IV. SUMMARY

We have investigated the effects of confinement and built-in strain on the electronic subband structure of nanoscale InP islands embedded in an $In_xGa_{1-x}P$ matrix using photoluminescence at high pressure and photoreflectance at ambient conditions. For pressures above the conduction-band Γ-X crossover in the InP islands and barrier material two emission bands are observed in the PL spectra of the 3 ML sample, which are associated with indirect recombination processes from the conduction X point to heavy holes at Γ of the islands and the matrix. From the energy difference of these PL bands we have estimated the valence-band offset for the strained InP/$In_xGa_{1-x}P$ heterojunction to be 80±15 meV. For a sample of 7 ML nominal InP thickness the indirect emission from the islands is no longer observed. This is a consequence of the larger relaxation of the built-in stress that occurs for larger-size islands. Due to the lower stress state in this case the X conduction-band edge of the larger InP islands lies above the X-point energy of the barrier material. Photomodulated reflectivity spectra measured at ambient conditions exhibit additional features which correspond to optical transitions between confined electron and heavy-hole states of the InP islands with subband index n=2. The interpretation of the experimental results in terms of effective-mass calculations of the confined levels in quantum wells allows us to separate in first approximation the effects of quantum confinement and strain for the InP island system.

ACKNOWLEDGMENTS

We thank W. Dieterich, U. Oelke, and U. Engelhardt for expert technical assistance. S.V. acknowledges financial support from the Max-Planck-Gesellschaft.

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*Permanent address: Physics Department, Aristotle University of Thessaloniki, Greece.

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