Optical evidence of the direct-to-indirect-gap transition in GaAs-AlAs short-period superlattices

G. Danan, B. Etienne, F. Mollot, and R. Planel
Laboratoire de Microstructures et Microélectronique, Centre National de la Recherche Scientifique, 196 Avenue H. Ravera, F-92220 Bagneux, France

A. M. Jean-Louis, F. Alexandre, B. Jusserand, G. Le Roux, J. Y. Marzin, H. Savary and B. Sermage
Laboratoire de Bagneux, Centre National d'Etude des Télécommunications, 196 Avenue H. Ravera, F-92220 Bagneux, France
(Received 6 October 1986)

We have studied electronic properties of GaAs-AlAs short-period superlattices grown by molecular-beam epitaxy. A direct-gap to "indirect"-gap transition has been evidenced through optical experiments on a large number of samples. It also corresponds to a type-I to type-II superlattice transition. Our results are in good agreement with an envelope-function description applied to each extremum of the host-material band structure. As a result of spatial transfer of electrons in AlAs, we have obtained an accurate value of the offset parameter $\Delta E_c^{\Gamma}/\Delta E_g^{\Gamma}=0.67$.

I. INTRODUCTION

The $Ga_{1-x}Al_xAs$ alloy is now commonly used as the large-gap material in epitaxial microstructures on GaAs. But the growth of such alloys remains difficult in molecular-beam epitaxy (MBE), especially from the point of view of surface and interface roughness. Moreover, the doping of this alloy with high Al content introduces deep centers responsible for persistent photoconductivity (so-called *DX* centers). Thus it has been suggested that the substitution of short-period superlattices (SPS's) could solve many problems, and now such SPS's are often included in microstructures.[1-4] However, little has been published on the fundamental electronic properties of these "new" materials since the pioneering work of Gossard *et al.*[5,6]

In this paper, our purpose is to present some of these properties obtained from systematic optical studies of a large number of samples. We shall emphasize the direct-to-indirect-gap transition when the AlAs concentration is increased, which is expected in SPS's as it is observed in disordered alloys. In Sec. II, we present our calculation of the various SPS energy gaps based on the envelope-function theory. Direct, "pseudodirect," and indirect gaps are found. Experimental results obtained through photoluminescence (PL), excitation spectra of PL, measurements of PL decay time, and PL under hydrostatic pressure are given in Sec. III. In Sec. IV we show that the fit of experimental results to theoretical curves can provide an accurate value of the still-questioned offset parameter.

II. ENVELOPE-FUNCTION APPROACH

In the envelope-function framework,[7] the wave function built from the host-material electron or hole states around an extremum of the band structure can be written as

$$\psi(\mathbf{r})=(S)^{-1/2}u_0(\mathbf{r})e^{i\mathbf{k}_\perp\cdot\mathbf{r}_\perp}F(z)\ , \tag{1}$$

where $\mathbf{r}_\perp=(x,y,0)$, $\mathbf{k}_\perp=(k_x,k_y,0)$, and S is the surface of the sample; u_0 is the periodic part of Bloch function at the extremum of interest.

$F(z)$ is the envelope function along the [001] axis (SPS growth axis). For a SPS with a large number N of periods, following Bloch theorem, $F(z)$ can be developed as

$$F(z)=(N)^{-1/2}f(z)e^{iqz}\ ,$$

where q is the SPS momentum along the growth axis and $f(z)$ is periodic with the period P of the SPS.

The envelope-function approximation, related to the Kronig-Penney model, has been applied by many authors to GaAs-$Ga_{1-x}Al_xAs$ superlattices. In the usual case where x is less than 0.4, the ternary alloy is a direct-gap semiconductor and therefore the SPS electronic states built from the Γ minima always lie at lower energy than the states built from the X minima of the zinc-blende Brillouin zone (BZ). In the present case, AlAs is the barrier material, which causes the maximum confinement of Γ-like states to increase. For thin GaAs layers, we found it may cross over the X states. Moreover, for these X states, the AlAs slab becomes the potential well (Fig. 1), at least for the typical offset values which are now commonly admitted. We define, as do many authors, the offset parameter Δ as the conduction-band discontinuity at the Γ point between the two materials divided by the band-gap discontinuity. The spatial transfer of electrons in AlAs occurs if Δ is less than $\Delta_c=0.84$ (using the band-gap energies listed in Table I). For $\Delta=\Delta_c$, there is no conduction-band discontinuity at the X point between GaAs and AlAs. This is the situation studied in Refs. 8 and 9.

To describe such a situation, we built SPS electronic states using the envelope-function formalism around X and L minima, as usually done around Γ minima of the host materials. This method is questionable for very thin layers, and no kind of mixing between Γ-like and X-like

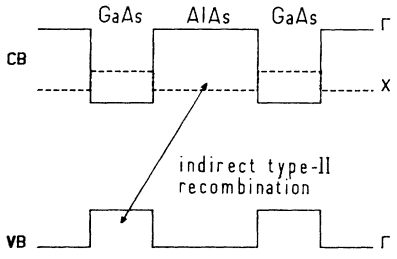

FIG. 1. Solid line represents the extrema of conduction and valence band of each bulk material at Γ and dashed line is the bottom of conduction band at X. In this picture, the offset parameter is equal to 67%.

states can be described, as it is in more sophisticated methods.[8–11] However, we found a rather good agreement with experimental data, as we shall see.

At X and L points, the effective mass tensor is anisotropic and the confinement energy must be calculated using masses along the [001] direction. The other tensor components determine the perpendicular motion. We point out that the difference between the values of the transverse and longitudinal mass will lead to a splitting of the energy levels associated with the X minima.

Since we investigate the electronic structure of the SPS through optical experiments, we have calculated the interband optical matrix element. Considering that the envelope function is slowly varying, and neglecting the dipole between envelope functions, we may write it as

$$M_{c,v}(\mathbf{k}_\perp,\mathbf{k}'_\perp,q,q') = \langle u_c \mid \mathbf{p} \mid u_v \rangle \delta(\mathbf{k}_\perp,\mathbf{k}'_\perp)\delta(q,q') \times \int f_c^*(z) f_v(z) dz \ . \quad (2)$$

The first term is the usual dipolar matrix element between conduction and valence bulk states. The overlap integral between envelope functions has been separated into three terms.

We now discuss the following:

(i) The dipolar matrix element $\langle u_c^X \mid \mathbf{p} \mid u_v^\Gamma \rangle$ should be smaller than $\langle u_c^\Gamma \mid \mathbf{p} \mid u_v^\Gamma \rangle$ because of the symmetry of the atomiclike function at the edge of the bulk crystal BZ.

(ii) The $\delta(\mathbf{k}_\perp,\mathbf{k}'_\perp)$ term expresses the conservation of momentum parallel to the layers. This selection rule should remain valid in a real superlattice. We deduce that optical transitions from valence Γ-like to conduction L-like states are "strongly forbidden," that is, they should involve localized impurity states or require phonon assistance as in bulk indirect-gap materials. The same applies to states constructed on [010] and [100] X minima of the zinc-blende reciprocal space.

(iii) The $\delta(q,q')$ term expresses the conservation of quasimomentum perpendicular to the layers, in the SPS reciprocal space. From this point of view, the Γ-like to Γ-like energy gap is obviously direct. The energy gap between Γ-like valence states and X[001]-like conduction states is also direct, *if* the superperiod of the SPS includes an even number of zinc-blende elementary cells: in this case, the wave vector of the X extrema maps onto the center of the SPS Brillouin zone. Strictly speaking, this term should forbid such transitions in SPS with an odd period. Contrasting with the $\delta(\mathbf{k}_\perp,\mathbf{k}'_\perp)$ selection rule, we think that the $\delta(q,q')$ selection rule should be relaxed,

TABLE I. GaAs and AlAs parameters used in this study. Most data are low temperature values. They are taken from the following sources: *Semiconductors, Physics of Group IV Elements and III-V Compounds*, edited by O. Madelung, and Landolt-Börnstein, III/17a (Springer-Verlag, Berlin, 1982) and S. Adachi, J. Appl. Phys. **58**, R1 (1985).

		GaAs	AlAs
Band-gap and spin-orbit splitting energies (eV)	$E_{g,\mathrm{dir}}(\Gamma_{8v}-\Gamma_{6c})$	1.519	3.1
	$E_{g,\mathrm{ind}}(\Gamma_{8v}-X_{6c})$	1.98[a]	2.23
	$E_{g,\mathrm{ind}}(\Gamma_{8v}-L_{6c})$	1.81[a]	2.5[b]
	$\Delta_0(\Gamma_{15v})$	0.341	0.3
Conduction-band effective masses (units of m_0)	$m_n(\Gamma)$	0.067	0.13
	$m_n(X)$ along Δ: m_t	0.23	0.19
	m_l	1.3	1.1
	$m_n(L)$ along Λ: m_t	0.07	0.1
	m_l	1.9	1.9
Valence-band effective masses (units of m_0)	m_{hh}	0.45	0.5
Offset parameter	$\Delta E_c/\Delta E_{g,\mathrm{dir}}=0.67$		
	$\Delta E_v=0.53$ eV		

[a]Parameters given at 110 K.
[b]Parameters given at 300 K.

otherwise it will be difficult to observe experimentally in a real SPS. As a matter of fact, it requires that the coherence of the wave function is maintained over several periods for Γ-like valence *and* *X*-like conduction states, both heavy-mass extrema in the zinc-blende BZ, leading to very narrow mini-bands. As an example, in order to make the selection rule efficient in a low-temperature experiment, Γ-like holes and *X*-like electrons should thermalize towards their respective band extremum in the SPS Brillouin zone, before recombination occurs. This is unlikely to happen for such heavy particles and we think that some experimental "evidences" of the direct character of SPS reported in literature are questionable.[3]

(iv) The last term of (2) expresses the overlap of electron and hole periodic parts of the envelope function. It is close to 1 in type-I SPS, where both ground states are essentially localized in the same layer. But it is much weaker, and more dependent on the structure, in a type-II SPS. This applies to the Γ-like valence to *X*-like conduction transitions, since the final state is essentially confined in AlAs layers. We think this is an essential reason for these transitions to be weaker than in the above-mentioned Γ case, even though they may be, strictly speaking, direct transitions.

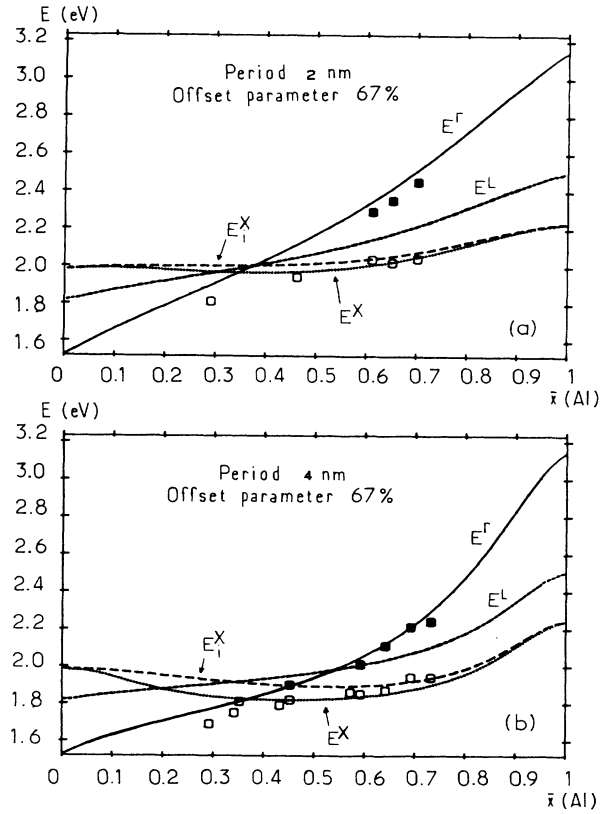

FIG. 2. Calculated energy gaps of GaAs-AlAs SPS. The curves are plotted as functions of x for $P=2$ nm in (a) and $P=4$ nm in (b). Experimental results are taken from samples with period close to the nominal 2 or 4 nm value and interpolated to be compared to the theoretical values, □: photoluminescence energy at 1.7 K. ■: experimental absorption threshold obtained through PLE at 1.7 K.

To summarize this discussion, we can assert that the SPS gap corresponding to the two *X* valleys along the [001] axis is "pseudodirect," since the one-photon transition is only weakly allowed. In addition, we presume the parity of the number of monolayers will not actually affect the intensity of corresponding optical transitions. Transitions involving *L*-like states and the four remaining *X*-like states are indirect since the electronic transverse momentum never vanishes and the condition $\mathbf{k}_\perp=\mathbf{k}'_\perp$ cannot be fulfilled.

We have calculated the SPS energy states built from Γ, *X*, and *L* minima in the envelope-function approximation, using a nonparabolic band structure in Γ (three-band Kane model), and a parabolic model for *X* and *L* minima and the heavy-hole valence band, for both GaAs and AlAs. The different parameters used in the calculation are shown in Table I.

In this paper, we shall discuss the results as a function of the following structure parameters: the period $P=L_{\mathrm{GaAs}}+L_{\mathrm{AlAs}}$ and the average aluminum concentration $x=L_{\mathrm{AlAs}}/P$. This is justified by the use of SPS as "pseudoalloys." In Fig. 2, we plotted representative results of calculated SPS energy gaps E^Γ, E^X (pseudodirect gap), E_i^X and E^L (indirect gaps) as a function of x for two different periods P, the offset parameter $\Delta=\Delta E_c^\Gamma/\Delta E_g^\Gamma$ being fitted to 67% as justified below. For high enough x, the lowest energy gap appears to be E^X. These are the structures we shall briefly name "indirect" in the following, to stress the similitude with disordered alloys. Let us recall that electrons and holes ground states are then separated in real space. As a consequence, one may expect that the "direct-to-indirect-gap" transition is also a type-I to type-II transition. Such a spatial transfer has been suggested in other structures.[12–14]

III. EXPERIMENTS

A. Growth and characterization

All the samples (typically 50) were grown by molecular-beam epitaxy (MBE):

1*st* series→$T_s=600$ °C P,x variable, $P\leq 20$ nm

2*nd* series→$T_s=650$ °C P,x variable, $P\leq 20$ nm

3*rd* series→$P=4$ nm T_s,x variable

(T_s is the temperature of the GaAs substrate during the growth).

They have been characterized by x-ray diffraction and some of them by Raman scattering. It revealed the good crystallographic quality of most samples and the reproducibility of the growth conditions. Except for a few poor quality samples which we excluded, the three series exhibit the same behavior with respect to the direct-indirect transition.

B. Photoluminescence

We performed photoluminescence (PL) experiments at 1.7 K using the 514.5- or 488.0-nm lines of a cw Ar^{2+} laser. Each sample was investigated and the PL linewidth provided some confirmation about the crystallographic

quality. Because of the large number of available samples, we have been able to classify them with respect to the features of their spectrum. Representative results are shown in Fig. 3.

In the structures expected to be direct within our above-mentioned calculation, we most often get one main intense and sharp line [Fig. 3(a)]. For some samples, the PL efficiency is very high: typical spectra are recorded with exciting power as weak as 1 mW/cm.[2] The full width at half maximum FWHM ranges typically from 0.6 to 7 meV; no shift is observed when increasing the excitation power; the line is presumably due to excitonic recombination. The PL energy is in good agreement with the computed value; as expected, it strongly depends on the structure parameters P and x (Fig. 2). Some poorer quality samples showed also a broader line at lower energy (several meV below the band gap) that we attributed to donor-acceptor recombination.

As a matter of fact, these direct structure spectra look very similar to the PL spectra of classical multilayer structures GaAs-$Ga_{1-x}Al_xAs$. In very-short-period superlattices, the coupling between neighboring wells depending on the AlAs slab width is observed by measuring the lowering of the PL energy.

In "indirect" structures, the PL efficiency is often smaller, typically 2—4 orders of magnitude when exciting light energy is lower than E^{Γ}. The spectra exhibit several lines with comparable intensities and energies separated by 20 to 30 meV [Figs. 3(b) and 3(c)]. To our knowledge, this is the first report of such structured spectra in GaAs-AlAs superlattices. As expected from the above-mentioned calculation, the energy of these lines is much less dependent on the Al concentration in a given constant-P series. This may be considered as a good evidence of the spatial separation of the recombining particles. We presume we observe the recombination from exciton states associated with the pseudodirect gap, possibly phonon assisted and impurity related. But since the theoretical splitting between E^X and E_i^X is as small as 20 to 60 meV, a more precise assignment of the different lines would require sophisticated experiments and is beyond the scope of this paper. The sample of Fig. 3(b) ($P=9.8$ nm and $x=0.7$) is well described by the envelope-function approximation. The confinement energies are small and the experimental PL energy provides a good determination of the offset parameter. This contrasts with the $P=2.6$ nm, $x=0.9$ sample [Fig. (3c)], for which the envelope-function approximation is highly questionable.

At higher temperature, the relative intensity of the Γ-Γ line increases and at room temperature, the direct recombination is essentially observed (Fig. 4).

C. Excitation spectra

Absorption experiment is, in principle, a straightforward test for the direct-indirect transition. However, the measurement requires a local etching of the GaAs substrate which may modify the strain field in the layer. In addition, interferences effects complicate the treatment of the data. Three indirect type samples were investigated at 77 K and both direct and indirect energy gaps were observed and measured. Actually, the excitation spectrum of photoluminescence (PLE) has appeared to provide the same essential information as absorption. We used a high-pressure Xe lamp and a simple monochromator which allow us to explore a large range of wavelengths from 820 to 380 nm. Two representative spectra are shown in Fig. 5.

In the direct-gap structures [Fig. (5a)], the PL intensity is non-negligible for any exciting energy above the PL line. It confirms the direct character of the energy gap and the intrinsic nature (or related to shallow impurities) of the PL.

In indirect structures [Fig. (5b)], the PL intensity is very weak for every exciting energy ranging between the indirect- and the direct-gap energies, which evidences the much weaker absorption coefficient. In such structures,

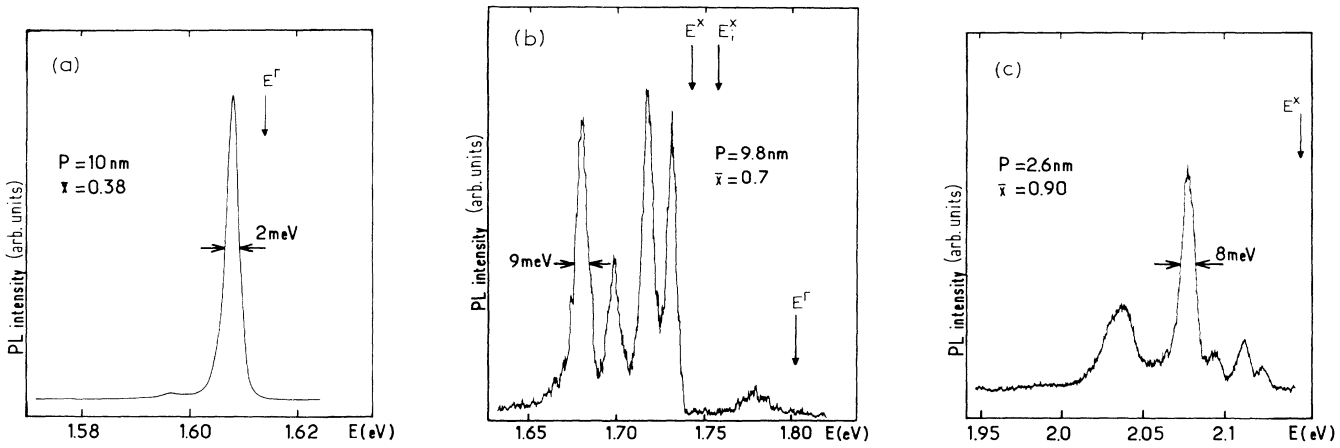

FIG. 3. (a) Photoluminescence spectrum of a representative direct sample. The typical exciting power is 1 mW/cm^2. (b), (c) Photoluminescence of two indirect samples with very different structure parameters. In (b), the line at 1.78 eV is the Γ-Γ recombination. All these spectra are obtained at 1.7 K. Arrows indicate calculated energy gaps.

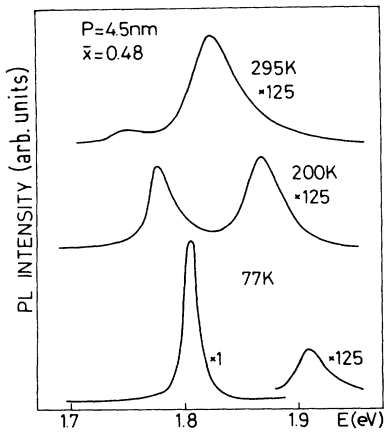

FIG. 4. Temperature dependence of an indirect PL spectrum at 77, 200, and 300 K. Both direct- and indirect-energy-gap recombinations are observed.

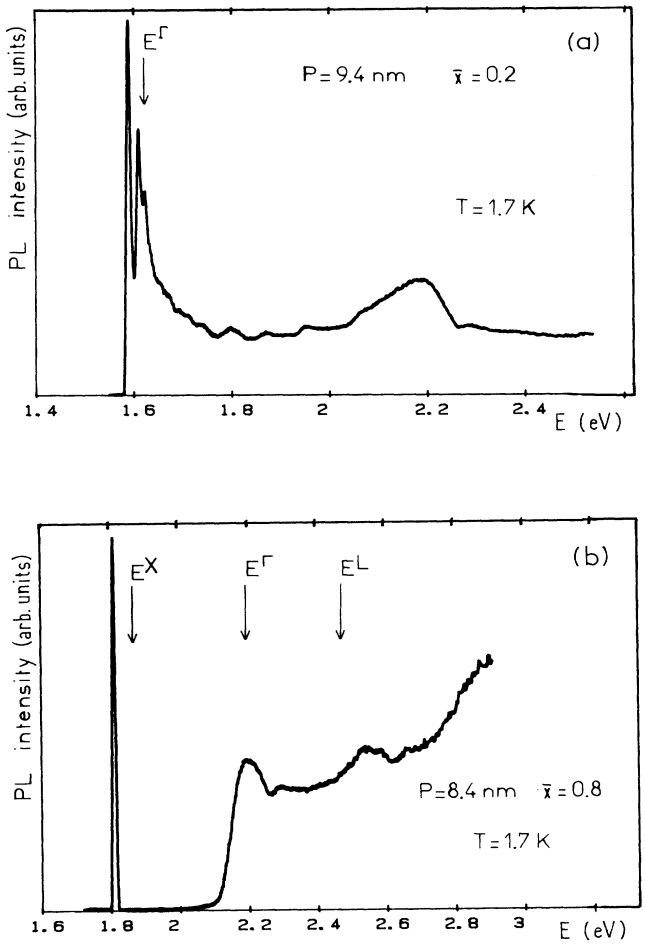

FIG. 5. Luminescence excitation spectra of representative direct (a) and indirect (b) samples at 1.7 K. The sharp low-energy peak corresponds to luminescence. Calculated energy gaps are pointed out.

both E^X and E^Γ values are provided in the same experiment.

Because of the striking qualitative difference between the two spectra, we found PLE to be an easy and rather unambiguous criterion to classify our structures. Obviously, the assignment of the SPS situated in the crossover region requires more sophisticated experiments, and may even be meaningless.

D. Complementary experiments

We performed measurements of PL decay time on ten selected samples. We used as exciting source, a cavity damped Ar^{2+} laser and processed the PL signal through a digital boxcar integrator. In indirect-type samples, as expected from the structure parameters, we measured lifetimes ranging from 40 to 100 nsec. In samples expected to be direct, the lifetime was shorter than our experimental resolution (20 nsec). No systematic study has been performed.

We also performed optical measurements under hydrostatic pressure. Due to the opposite shifts of Γ and X conduction extrema, such experiments allow us to determine the nature of the SPS energy gap. Photoluminescence measurements at 300 K and under hydrostatic pressure up to 6 kbar were carried out for five selected indirect samples (Fig. 6). As expected, the line corresponding to E^Γ is shifted to the higher energies with a coefficient $dE^\Gamma/dp \simeq 10$ meV/kbar. The E^X line is slightly shifted to the lower energies. In the same time, the relative intensity of the indirect transition is increased. As a consequence, near the crossover point, the indirect recombination line appears more clearly under hydrostatic pressure.

IV. DISCUSSION

The offset parameter is the only adjustable one in our calculation. Moreover, the E^X transition energies calculated in type-II SPS are very sensitive to the offset value, because recombination occurs "across" the GaAs-AlAs interface (Fig. 1). This situation contrasts with standard determinations of Δ in GaAs-$Ga_{1-x}Al_xAs$ structures.

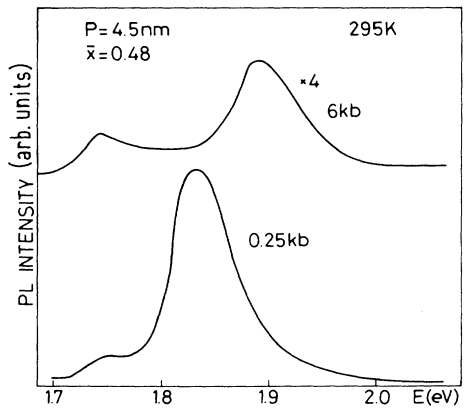

FIG. 6. Photoluminescence spectra of a representative indirect sample under hydrostatic pressure at room temperature.

This sensitivity provides an accurate fit to optical data. This is especially true in large-P and high-x type-II SPS, where the E^X energy is close to its lower limit value:

$$E^X_{\text{limit}} = E^X_{\text{AlAs}} - (1-\Delta)(E^\Gamma_{\text{AlAs}} - E^\Gamma_{\text{GaAs}}) \simeq 1.7 \text{ eV}$$

and $\Delta = 0.67$.

Actually, our determination is essentially limited by the poor amount of knowledge of AlAs parameters, primarily band gap energies.

In conclusion, we have studied a representative set of GaAs-AlAs SPS's. Their optical properties allow us to distinguish direct type-I on the one hand, pseudodirect, or indirect type-II, on the other hand. An envelope-function calculation around each extremum of the host material band structure gives a fairly good description of this experimental feature, and a quantitative agreement with the measured energy-gap values. The calculated crossover curve which separates the two domains in a P versus x graph is plotted in Fig. 7, and investigated samples have been marked on it. The first domain includes direct type-I samples; it corresponds, roughly speaking, to $x \leq 0.35$ *or* $L_{\text{GaAs}} \geq 4$ nm. The other domain includes SPS with optical properties analogous to those of indirect-gap materials, although they may be considered as "pseudodirect." Some ambiguous samples lie in the crossover region. Our determination $\Delta = 67\%$, which agrees with recent results in GaAs-$Ga_{1-x}Al_xAs$ systems, corresponds also to the best crossover curve which separates the direct and indirect regions.

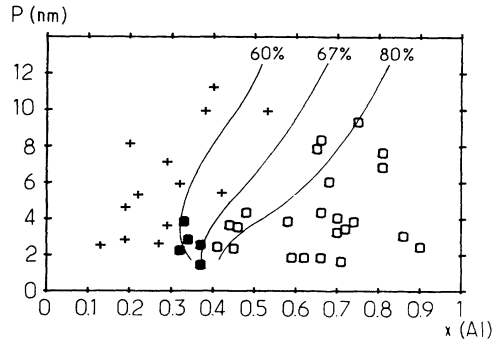

FIG. 7. All investigated samples are displayed on this P versus x graph. Following our experimental criteria, we distinguish the direct (+) from indirect (□) and ambiguous (■) ones. The theoretical crossover curves for some different values of Δ are plotted.

Our results should disappoint with respect to the ability to make direct pseudoalloys with larger energy gap than in random alloys. But they could stimulate a revision of the theoretical problem[8,9] using, as an offset parameter, $\Delta = 0.67$.

ACKNOWLEDGMENTS

The authors especially thank D. Paquet and G. Bastard for helpful discussions. The Laboratoire de Microstructures et Microélectronique and The Laboratoire de Bagneux comprise Groupement Scientifique de Bagneux CNET-CNRS.

[1]K. Fujiwara, J. L. de Miguel, and K. Ploog, Jpn. J. Appl. Phys. **24**, L405 (1985).

[2]T. Baba, T. Mizutani, and M. Ogawa, J. Appl. Phys. **59**, 526 (1986).

[3]A. Ishibashi, Y. Mori, M. Itabashi, and N. Watanabe, J. Appl. Phys. **58**, 2691 (1985); A. Ishibashi, Y. Mori, F. Nakamura, and N. Watanabe, J. Appl. Phys. **59**, 2503 (1986).

[4]H. Sakaki, M. Tsuchiya, and J. Yoshino, Appl. Phys. Lett. **47**, 295 (1985).

[5]A. C. Gossard, P. M. Petroff, W. Weigmann, R. Dingle, and A. Savage, Appl. Phys. Lett. **29**, 323 (1976).

[6]J. P. van der Ziel and A. C. Gossard, J. Appl. Phys. **48**, 3018 (1977).

[7]G. Bastard, Phys. Rev. B **24**, 5693 (1981).

[8]J. N. Schulman and T. C. McGill, Phys. Rev. B **23**, 4149 (1981).

[9]W. Andreoni and R. Car, Phys. Rev. B **21**, 3334 (1980).

[10]K. B. Wong, M. Jaros, M. A. Gell, and D. Ninno, J. Phys. C **19**, 53 (1986).

[11]T. Nakayama and H. Kamimura, J. Phys. Soc. Jpn. **54**, 4726 (1985).

[12]T. J. Drummond and I. J. Fritz, Appl. Phys. Lett. **47**, 284 (1985).

[13]P. Dawson, B. A. Wilson, C. W. Tu, and R. C. Miller, Appl. Phys. Lett. **48**, 541 (1986).

[14]L. Brey, C. Tejedor, J. L. de Miguel, F. Briones, and K. Ploog, Proceedings of the 18th ICPS, Stockholm, 1986 (to be published).