Short-period GaAs-AlAs superlattices: Optical properties and electronic structure

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We report the results of low-temperature photoluminescence and photoluminescence excitation studies of short-period, $n=m$, $(GaAs)_n$-$(AlAs)_m$ superlattices fabricated by molecular-beam epitaxy. Values of n ranged between 2 and 8. We find that the smallest energy gap does not approximate to that of an $Al_{0.5}Ga_{0.5}As$ alloy until $n+m \leq 4$ monolayers. The limits of a simple Kronig-Penney model of the electronic states are explored in relation to our observations. For the direct gap, good agreement is achieved between experiment and theory down to $m=n \geq 4$ monolayers. The description of the "pseudodirect" gap breaks down at $n=m \sim 6$ monolayers. Reasons for the failure of the simple description are discussed.

INTRODUCTION

In spite of having received more than a decade of increasingly intense investigation, fundamental questions remain unanswered regarding the electronic properties of the archetypal heterojunction system of GaAs-(Al,Ga)As. In particular, our understanding of the electronic structure of GaAs-AlAs short-period superlattices, i.e., when the GaAs- and AlAs-layer thicknesses are smaller than ~ 10 monolayers, is somewhat hazy in a number of respects: How closely does the system approximate to that of the corresponding $Al_{0.5}Ga_{0.5}As$ alloy? From a spectroscopic viewpoint, is the lowest-energy transition direct, indirect, or pseudodirect and does it change as a function of layer thickness? How complete is our theoretical understanding of these structures?

From a theoretical point of view the question of the electronic structure of $(GaAs)_n$–$(AlAs)_m$ superlattices (SL's) has been attacked by a variety of methods from the simplest Kronig-Penney calculation,[1] through envelope-function-type calculations[2] to the sophisticated microscopic methods based on tight-binding,[3,4] empirical and self-consistent pseudopotentials,[5–7] and local-density[8] or augmented-spherical-wave calculations.[9] It is fair to say that there is no concensus amongst these calculations (sometimes even using the same method) as to the nature of the electronic structure of the $(n+m)$ SL as the number of monolayers n or m is varied. For example, Nakayama and Kamimura[7] have used a self-consistent pseudopotential scheme to predict that the (1 + 1) GaAs-AlAs SL has its lowest conduction-band state at the R point of the SL Brillouin zone, making the smallest gap indirect, while for $n=m=2$, 3, and 4, the lowest state is predominantly Γ-like in character and the SL's have a direct energy gap. In contrast, Andreoni and Car,[5] using a non-self-consistent, supercell, empirical pseudopotential scheme found that the band gap of the $n=m=1$, 2, 3, and 4 SL's were "pseudodirect" with the lowest state having predominantly the character of the folded X-point state. Andreoni and Car found a small shrinkage of the lowest gap between the (1 + 1) SL and the (4 + 4) SL of only 16 meV. Qualitatively these latter results are in accord with the effective-mass calculations presented here. In this simplest of the calculational schemes the lowest state for the $n=m$ SL, when $n=m \leq 10$, is also predicted to be the folded AlAs X state. Although the scale of the change of the pseudodirect gap is found to be about an order of magnitude larger, shrinking by ~ 120 meV between the (1 + 1) SL and the corresponding (4 + 4) system compared to the 16-meV variation found by Andreoni and Car.[5]

In this paper we report the results of low-temperature (≤ 8 K) photoluminescence (PL) and photoluminescence excitation (PLE) measurements made on short-period, nominally $n=m$, $(GaAs)_n$-$(AlAs)_m$ SL's grown by molecular-beam epitaxy (MBE). Values of n ranged between 2 and 8. The measurements are contrasted with other low-temperature PL observations on similar GaAs-AlAs short-period structures grown either by MBE (Refs. 10–14) or metal-organic chemical vapor deposition (MOCVD).[15,16] Some of this work[12] claims to present evidence supporting a change from a direct to indirect band gap with decreasing period, while other workers[15,16] studying nominally the same structures conclude that their observations are in accord with the PL expected from an $Al_{0.5}Ga_{0.5}As$ bulk specimen. The collected experimental results are also compared to our simple envelope-function[17] and effective-mass-type calculations of the subband edges of the Γ, folded X, and nonfolded X minima as the SL period $(n+m)$ is varied.

GROWTH DETAILS AND STRUCTURAL ANALYSIS

The samples studied here were all grown in a Varian Gen-II MBE system. Growth conditions were as close as reproducibly possible to those used previously.[18] All the layers were deposited on (001)-oriented semi-insulating GaAs substrates held at a nominal substrate temperature of 630 °C. The substrate was rotated during growth which was continuous. The growth sequence was as follows: (a) a 1-μm GaAs buffer, (b) ~ 1 μm of alternating layers of GaAs and AlAs (the SL region), and finally (c) a 0.1-μm GaAs capping layer. None of the layers was intentionally doped. In the SL region of the sample we

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aimed to keep the GaAs and AlAs layer thicknesses equal, i.e., $n=m$. Values of n ranged between 2 and 8 for the samples to be discussed here.

All the samples have been examined using x-ray diffraction techniques. A diffractometer scan along (001) gave satellite peaks in the vicinity of (000) and (00L) Bragg reflections. The satellite peak positions and intensities allow one to comment on the periodicity of the SL and on the interface sharpness, respectively. The high-resolution diffractometer profile close to the (115) reflection was compared with simulated profiles using dynamical diffraction theory to yield the average mole fraction, x, of the SL.[19] Measurements[20] on the specimens studied here revealed that all the samples had an average Al fraction close to 0.5, with average periods within 0.5 monolayers (ML's) of their nominal values. However, preliminary investigations of the number and strength of satellite peaks for these samples shows some evidence for an effective variation in the Al fraction at the interfaces. This effect is more pronounced for the (2 + 2) and (4 + 4) samples. That such an effective grading exists is not at all surprising when one considers that the samples have been grown without any interrupts.

Before proceeding it is as well to be aware of the dangers of only a cursory glance at the information provided by x-ray analysis. Let us suppose that we have grown a thin sample which contained 50% of layers with a period of 5 + 5 and 25% each of periods 4 + 6 and 6 + 4; then analysis of only the position of satellite peaks would not reveal the changes in individual layer thicknesses but reveal only that the sample had a periodicity of 10 ML. Also, the average Al fraction remains at 0.5 although it clearly varies throughout the structure. Detailed modeling of both intensities and positions of satellite peaks near, for example, the (002) reflection and of the double crystal diffractometer patterns would be necessary to reveal such variations.[21] Such detailed, full modeling of the scattering process is not usually attempted and like other investigators we rely only on information about periodicity and average Al fraction x to characterize the structural integrity of our as-grown SL's.

PHOTOLUMINESCENCE: EXPERIMENTS AND RESULTS

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded with the samples mounted on the cold finger of a variable temperature (4–300 K), continuous flow cryostat. For the PL measurements the samples were excited with either the 5145-Å line of an Ar^+ laser or at 5713 Å by an Ar^+ pumped dye (Rhodamine-6G) laser. The same dye laser arrangement provided the tunable source for the PLE measurements. The luminescence was collected and analyzed by a double-grating monochromator and detected with a cooled GaAs photomultiplier and associated photon-counting electronics. We report results on $(GaAs)_n$-$(AlAs)_m$ SL's where $n=m=2$, 4, 5, 6, and 8 monolayers.

Figure 1 shows the 5-K PL and PLE spectra from the (6 + 6) sample. For convenience we label the spectral regions (a), (b), and (c). Regions (a) and (b) illustrate the PL and PLE associated with the pseudodirect X-Γ transitions, while region (c) shows the PLE spectrum in the vicinity of the direct Γ-Γ transition. The PL spectrum in Fig. 1(a) was recorded using an excitation wavelength of 5145 Å. Theoretically, we anticipate that the lowest conduction-band state of this sample would be at X_z, in AlAs, and that the thickness of the GaAs is sufficient to allow only weak coupling of the states in adjacent AlAs layers. The sample is thus akin to the "type-II" samples previously studied by ourselves[22,23] and by Finkman and co-workers[14,24] and we continue to assign the emission, at 1.8990 eV, to the recombination of localized excitons built from electron states at X_z in AlAs and holes at Γ in GaAs. Setting the detection energy at 1.902 eV and performing PLE over the energy range spanned by (b) reveals a distinct feature at ~ 1.9265 eV. At this energy excitons are being created via states at the X_z minima. As in the previous study[23] of the nature of the pseudodirect transition, its localized character is inferred from the temperature dependence of the PL and PLE peaks. The localization energy of the exciton, deduced from the shift between PL and PLE peaks, is about 26 meV for this sample. Continuing to scan the excitation source over region (c) reveals a strong rising edge, whose midpoint is close to 2.06 eV. No clear excitonic, Γ-Γ, peaks are discernible for samples of this dimension and smaller, in accord with measurements reported earlier by Nagle and co-workers.[13]

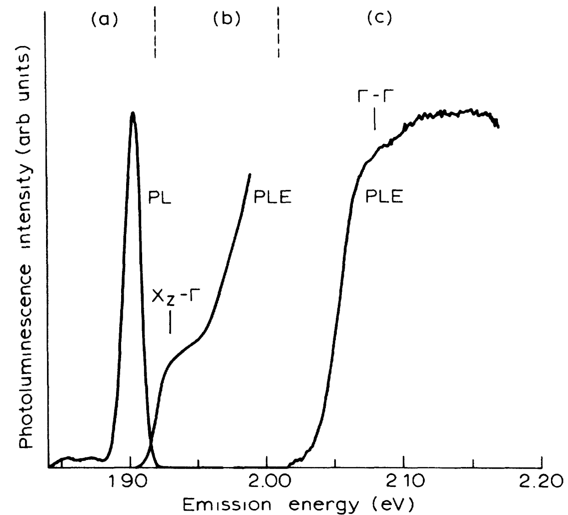

FIG. 1. Low-temperature (~ 5 K) photoluminescence (PL), region (a), and photoluminescence excitation (PLE) spectra, regions (b) and (c), of the (6 + 6) GaAs-AlAs superlattice. Note that there is an increase in the gain of the detection system between regions (c) and (b).

The absence of distinct light- and heavy-hole excitons in the (6 + 6) sample can be understood by reference to our observations on a sample only 2 ML larger, i.e., the (8 + 8) SL.[22] PLE in the region of the Γ-Γ transition on the (8 + 8) sample does reveal two, fairly broad peaks associated with the fundamental heavy- and light-hole exci-

tons. The width of these resonances is presumably controlled to some extent by the degree of broadening introduced by intrawell width fluctuations. This effect is most pronounced on the electron component due to its far larger confinement energy. For example, a 1-ML decrease in well width for an isolated 8-ML GaAs well corresponds to an increase in the electron confinement energy of ~ 50 meV, while the same change for a 6-ML sample is ~ 70 meV. Presumably, in the $(8+8)$ sample the separation between the light- and heavy-hole confinement levels (~ 75 meV) is sufficiently large to offset any broadening and distinct peaks are observed. In the $(6+6)$ sample however, increased broadening due to larger intrawell changes in confinement energy and the decreased splitting of light and heavy holes (~ 65 meV) due to interwell coupling is sufficient to render the individual resonances unresolvable.

We now turn to the $(5+5)$ and $(4+4)$ SL samples. For illustrative purposes, we concentrate on the $(4+4)$ sample, but almost all the remarks could be made equally well about the $(5+5)$. The 5-K PL and PLE spectra from the $(4+4)$ sample are displayed in Figs. 2(a)–2(c). The PL spectrum from this sample is noticeably different from the wider $(6+6)$ and $(8+8)$ samples. Three distinct peaks are seen and we believe that the highest-energy line is intrinsic in nature, again involving the X_z-Γ transition, but that the two lower-energy features are most likely extrinsic in origin. The reasons for such assignments are given in the course of the discussion below.

Setting the detection energy at 2.015 eV to record a PLE spectrum over the energy range of region (b) revealed a distinct peak at 2.0410 eV and another feature at higher energy. This higher-energy feature is on a sharply rising edge associated with the direct, Γ-Γ, transition so without deconvolution of the spectra its precise position is difficult to gauge; we estimate it to be at ~ 2.1 eV. The peak at 2.041 eV we assign to the creation of X_z-Γ, free excitons. We can only speculate as to the origin of the

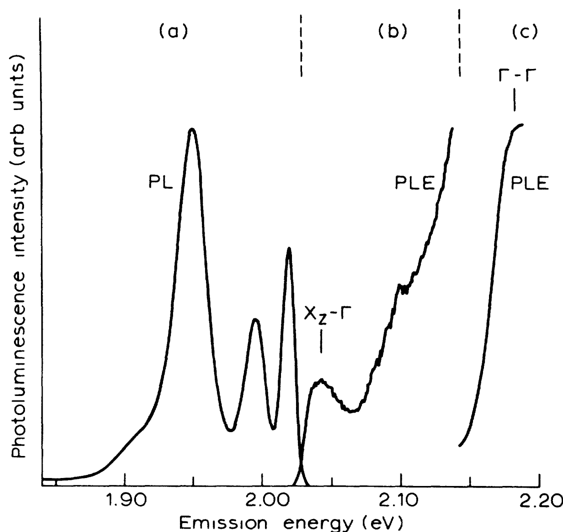

FIG. 2. Same as for Fig. 1 but for the $(4+4)$ GaAs-AlAs superlattice.

feature near 2.1 eV. Calculations of the subband energies show that there are no higher confined states either at X or at Γ for both electrons and holes for a sample of this dimension. So transitions involving confined excited states can be ruled out. The calculated X_z-X_{xy} splitting for this sample is 40 meV, so a X_{xy}-Γ excitonic transition is a possibility. However, the observed splitting is somewhat larger, even given the relatively poor estimate of its position and the shape is suggestive of a peak rather than an edge, making a transition involving the X_z state more likely; the most probable being that from a light-hole state at Γ to the X_z minima. Although, once more, the calculated light-to-heavy-hole splitting of ~ 40 meV is a bit small to be definite about this assignment. Continuing the PLE scan to higher energy reveals a sharply rising edge whose onset is close to 2.15 eV with the top of the step being close to 2.180 eV. This strong increase in PLE signal is once more attributed to the direct Γ-Γ absorption in the SL.

Let us return now to the assignment of the features in the PL spectrum of the $(4+4)$ sample. We have asserted above that the highest-energy peaks is an intrinsic X_z-Γ transition, while the two features at 1.9940 and 1.9478 eV are extrinsic in origin, rather than, for instance, parts of the sample with a different GaAs-AlAs period. Evidence supporting these assignments comes from a number of observations such as the temperature dependence of the individual emission lines. The X_z-Γ line moves to higher energy initially (up to about 40 K) after which it closely tracks the temperature dependence of the band gap, in line with previous observations on type-II systems.[23] In contrast, the two lines at lower energy move rapidly further down in energy at a rate in excess of the temperature dependence of the gap. This observation is qualitatively the same as that reported by Finkman *et al.*[24] for the temperature dependence of the "D" line seen in their "indirect" GaAs-AlAs samples. Like these authors, we too believe that this temperature dependence argues strongly in favor of the transition involving some as yet unidentified defect or deep impurity. Secondly, we measured the power dependence of the low-temperature emission spectrum, being careful to maintain power densities below ~ 20 W cm^{-2} so as to avoid sample heating. The intensity of the highest-energy line increases in a linear fashion with increasing excitation power, while the intensities of the lower-energy lines begin to saturate at around 8 W cm^{-2}. Again, these observations are consistent with the above assignments of the PL features. Finally, if PLE spectra are recorded with the detection energy set at the peak of either of these two lower-energy features then the strong Γ-Γ transition is no longer present. This is contrary to one's expectation if the peaks were intrinsic, since detection at 1.994 eV should result in a PLE spectrum similar to that of Fig. 3(c) but with an additional strong feature at lower energy due to the creation of free excitons, "Stokes shifted" to higher energy from the detection energy.

Turning now to the 5-K PL spectrum for the $(2+2)$ sample which is shown in Fig. 3 and is similar to that reported by Nagle *et al.*,[13] we identify three distinct peaks riding on a large, probably impurity-related background.

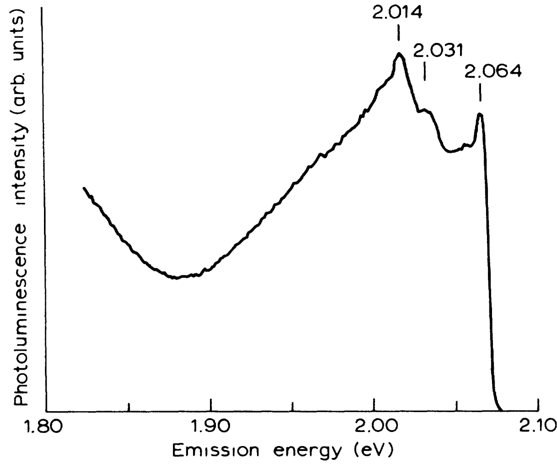

FIG. 3. Low-temperature ($\sim$5 K) photoluminescence spectrum of the (2 + 2) GaAs-AlAs superlattice.

The highest-energy peak is most likely excitonic in origin while the two peaks at lower energy would be consistent with being bulk phonon replicas of the excitonic feature.[16] This spectrum most closely resembles that of an $Al_{0.5}Ga_{0.5}As$ alloy. That this should be the case can once more be understood by considering the growth conditions. Remember that growth is continuous for these samples so that it is extremely unlikely that the interfacial regions can be considered to be extended flat areas. Most likely the in-plane extent of the interfacial islands is smaller than the scale of the excitonic probe and if we consider that the minimum step height is 1 ML then the now quasi-three-dimensional exciton is essentially sampling an alloylike region of the crystal. This effect, of course, becomes more pronounced as the layer dimensions become smaller, manifesting itself also in the x-ray analysis as a grading of the Al fraction at the interfaces.[20]

CALCULATIONS AND DISCUSSION

Our calculations of the subband structure of GaAs-AlAs, (001)-oriented multiple quantum wells and SL's have been made within the envelope-function approximation. We specifically concerned ourselves with the subband structure associated with the Γ point and X points. Coupling between the states belonging to different symmetry points in the Brillouin zone of the bulk was not considered. Any effects of elastic strain, due to the small difference in lattice constant between the binary compounds, were also neglected. (We return to this point below.) To proceed with the calculations we adopted a conduction-to-valence-band offset ratio of 67:33, in line with the most accurate optical determination of this quantity.[18,25] Neglecting any confinement effects and assuming this offset ratio of 67:33 makes the X point in AlAs the lowest X state at the GaAs-AlAs heterojunction. Within our simple model this means that (i) electrons at Γ see a Kronig-Penney potential whose size is determined by the Γ-Γ separation of the conduction-band extrema between GaAs and AlAs, while (ii) electrons at one of the X points experience a Kronig-Penney potential determined by the separation between the X point of AlAs and the X point of GaAs.

The lowest subband for the electron at the Γ point in the GaAs was calculated using our version of Bastard's implementation of the Kane model.[2] Nonparabolicity of the Γ electron band is included naturally in this model. Subband minima for the various X points were calculated by ensuring continuity of the envelope function and the product of $(1/m^*)$ and the derivative of the envelope function at each of the heterointerfaces. We neglected any complications associated with the "camel's back" structure of both GaAs and AlAs and assumed parabolic dispersion for an electron state located precisely at the X point. The effective masses used in the calculations are shown in Table I. We continue to use values of $0.34m_0$ and $0.094m_0$ for the heavy- and light-hole effective masses in GaAs. These are the values preferred by Miller *et al.*[26] and by ourselves[27] to describe the positions of the observed excitonic transitions in isolated GaAs-(Al,Ga)As multiple-quantum-well heterostructures. In particular the value of $0.34m_0$ was essential to fix the position of the HH3-E1 transition.[27] The continued use of both these values has recently been given additional support by a careful spectroscopic study of the dependence of observed excitonic transitions in isolated GaAs quantum wells fabricated on substrates with different crystallographic orientation.[28] The consequence of this study is the authors' proposal of a new set of Luttinger parameters to describe the valence-band anisotropy of GaAs, with the result that along the (001) direction the derived values of the heavy- and light-hole masses are $0.34m_0$ and $0.094m_0$, respectively.

Note that the anisotropic nature of the X minima means that those X minima which have a component of momentum parallel to the growth direction, (001) and labeled X_z, have a much larger confinement mass than those whose momenta lie in the layer planes, i.e., (100) and (010) which we label X_x and X_y. Often we will refer to the latter pair of states as X_{xy}. Some uncertainty exists in the literature as to the precise values of the X-point effective masses either in GaAs or in AlAs, however the important point to remember is that the longitudinal mass at the X point is large, whereas the transverse mass is small.

For the calculation we make here, the factor of almost 6 between the confinement mass of the X_z minimum

TABLE I. Effective masses in units of m_0 used in the model calculations.

	$m_e^{\Gamma}((001))$	$m_{hh}^{\Gamma}((001))$	$m_{lh}^{\Gamma}((001))$	$m_e^{X}((001))$	$m_e^{X}((010))$
GaAs	0.0665	0.34	0.094	1.3	0.19
AlAs	0.15	0.752	0.16	1.1	0.19

versus that of the X_{xy} minima ($1.1m_0$ compared to $0.19m_0$) means that the folded X_z state is *always* at a lower confinement energy than the unfolded X_{xy} states in any GaAs-AlAs multiple-quantum-well or SL system. This conclusion would be modified somewhat if the elastic strain between the AlAs and GaAs layers were important as has recently been suggested by Drummond and co-workers.[29] The lattice constant of AlAs is slightly larger than that of GaAs and as the layers are epitaxially deposited on a GaAs substrate then, for thin enough layers, the GaAs is unstrained and the AlAs layers are under biaxial compression in the layer plane. The shear component of the strain, parallel to the growth direction, splits the degeneracy of the X minima with the result that even in bulk material X_{xy} would be below the X_z minimum by about 16 meV, if one assumes that the deformation potentials of AlAs are similar to those of GaP.[29] Evidence for the existence of such an ordering of the states in wide ~150-Å AlAs layers has come recently from the magnetotransport measurements of Smith *et al.*[30] No quantitative information about the size of the strain splitting is available from this data, however. We should note that with decreasing AlAs thickness the effect of strain splitting would be quickly swamped by the confinement effect and the X_{xy} state would be raised most rapidly leaving X_z the lowest energy state. For $(GaAs)_m$-$(AlAs)_m$ SL's this happens when $m = 30$ ML. The difference in potential well depth between the X_{xy} and X_z states produced by the strain has an interesting consequence as the number of monolayers is further reduced; our prediction being that the lowest state for a (1 + 1), GaAs-AlAs SL would be the unmixed X_{xy} states; lying ~4 meV below the folded X_z state. We should, however, remember that the deformation potentials of the binary compound AlAs are not particularly well known, so that the exact strain splitting between the X states is somewhat uncertain. Aside from the interesting, predicted but probably undetectable,[9] realignment of the minima for the (1 + 1) SL, none of the observations we make below depend explicitly on the system being strained; so we leave it out of the calculation.

In Fig. 4 we show the calculated variation of the Γ-Γ, X_z-Γ, and X_{xy}-Γ subband-subband energy gaps as a function of the $(GaAs)_m$-$(AlAs)_m$ SL period ($2m$). Also shown for reference are the direct and indirect energy gaps of an $Al_{0.5}Ga_{0.5}As$ bulk sample. Γ refers to the lowest conduction-band state in the GaAs, while the X states refer to the minima in the AlAs layers. Also shown in this figure is a collection of the available spectroscopic data on $n = m$ GaAs-AlAs short-period SL's. We comment on the comparison of this data either with the theory, with our own data, or between sets of data below. As we noted earlier, we find the X_z state is always below the unmixed X_{xy} state and for periods smaller than 22 ML it becomes the lowest conduction-band state of the whole system[17] with the valence- to lowest conduction-band lineup taking on a staggered or type-II arrangement. Unlike the situation of fixed GaAs thickness and decreasing AlAs layer thickness[23] the $n = m$ SL can never revert back to a type-I or straddled arrangement for the valence- to lowest conduction-band lineup. From these calculations we can say that when the period of $n = m$, $(GaAs)_n$-$(AlAs)_m$ SL's is smaller than 20 ML we would expect to observe the allowed, no-phonon recombination of an electron of predominantly AlAs X character, i.e., folded X_z with a hole at the Γ point localized mainly in the GaAs layers and not an electron at the X_{xy} minima as suggested by Finkman *et al.*[14,24]

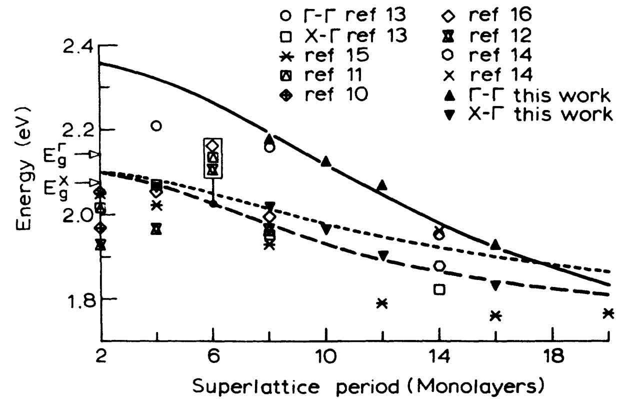

FIG. 4. Comparison between our model calculations of the principal subband-subband energy gaps of $(GaAs)_n$-$(AlAs)_n$ superlattices and a variety of available experimental data. The solid curve is the calculated Γ-Γ gap, dotted curve is the X_{xy}-Γ gap, and the dashed curve corresponds to the X_z-Γ gap. Also marked on the plot are the direct and indirect energy gaps of an $Al_{0.5}Ga_{0.5}As$ bulk sample.

Finkman and co-workers[14,24] cite the observed PL decay characteristics and the theoretical predictions of Ihm[31] as supporting their assignment. Discussion of the temporal behavior of the PL they observe has been made in other publications[32] and in the present context, i.e., considering the energy ordering of the states, we concern ourselves only with Ihm's calculation. Ihm's conclusion and arguments can be summarized as follows: for AlAs layers thinner than ~20 Å the X_z level is higher than the X_{xy}. The origin of the *lowering* of the X_{xy} state lies in the existence and strength of the superlattice potential, ΔV, and the interaction produced between the states X_x and X_y. This superlattice potential and the various mixings it produces are, of course, ignored in a simple model like the one we have used above. The coupling of the X_x and X_y states occur in the following manner:[24] X_x, (100), is degenerate with the point (101); this state can in turn be coupled to the X_y state (010) by a *bulk* reciprocal lattice vector. The X_x and X_y states are thus mixed by ΔV and their degeneracy split by an amount $2\langle 100 | \Delta V | 010 \rangle$. As pointed out by Ting and Chang[33] the mixing is a little more subtle than this and depends on the parity of the states X_x and X_y. For example,[33] if the AlAs layer thickness is an even number of ML's then the X_x and X_y states have the opposite parity and do not interact to lift their degeneracy. The interaction *only* occurs if the AlAs thickness is an odd number of monolayers.

Ihm[31] and Ting and Chang[33] do not disagree that in certain circumstances the degeneracy of X_x and X_y can be lifted with a subsequent lowering of the mixed X_{xy} state. Where these authors do disagree is in the size of the mixing. For their one-band, multiple-valley Wannier orbital model Ting and Chang[33] calculate the mixing to lower the confined state energy by no more than a few meV for a (5 + 5) $(Al_{0.25}Ga_{0.75})As$-AlAs SL, in all cases finding the X_z minima to be the lowest, whereas Ihm *states* that the mixing is sufficient to lower the mixed X_{xy} state below the X_z state. Ihm's assertion is based on his tight-binding calculations and local-density pseudopotential calculations, details of which are not presented in his paper. Due to computational complexity the latter can only be performed for small values of n and m, most likely no larger than $n = m = 4$. As we have noted above, similar theoretical methods often give contrasting results and here we have a good illustration. Nelson, Fong, and Batra[34] have also used a self-consistent pseudopotential scheme to study the electronic structure of short-period GaAs-AlAs SL's when $n = 2,3,4$. Unlike Ihm, these authors find that the lowest X state in the system is the folded X_z state. To be fair, however, one should acknowledge that it is only lower by ~ 10 meV when the accuracy of such calculations is probably ~ 100 meV. This criticism, with regard to accuracy, is relevant to all these microscopic calculations, including that of Ihm, and thus makes it hazardous to draw positive conclusions from them alone.

Intuitively, one feels that except for the shortest SL periods the lowest state of the GaAs-AlAs SL should be the folded X_z state, with the SL potential providing a relatively small perturbation on the energy of the X_{xy} states compared to their confinement energy. To some extent this picture is borne out in the ability to describe theoretically the spectroscopic data on type-II GaAs-AlAs quantum wells in terms of the folded X_z state being the lowest in the system[23] using the same calculation.

COMPARISON WITH EXPERIMENT

The energy positions of the direct Γ-Γ-related transitions and the X-related transitions are compared with our decoupled, X and Γ, Kronig-Penney-type calculations in Fig. 4. We have also plotted a large selection of other available data and marked the band-edge positions of the indirect, X, and direct gaps for an $Al_{0.5}Ga_{0.5}As$ alloy. All the Γ-related observations plotted refer to positions determined from PLE and are all most likely excitonic in origin. To compare with the calculated band-band transitions an additional binding energy, of the order of 10 meV,[35] needs to be added to the observations. On the other hand, the lower-energy peaks are all assumed to be intrinsic PL peaks. They all need to be corrected by a similar amount for the exciton binding energy[36] and in some cases by an additional amount to account for the localized nature of the emission[18]—a total correction of ~ 30 meV upward in some cases.

It is clear that the energy position of the Γ-Γ transitions is extremely well reproduced down to the (4 + 4) SL. Below (4 + 4) the experimental data is scarce, however the one reported measurement by Nagle *et al.*[13] lies well below both our calculations and similar ones made by these authors. It is extremely surprising that such a simple model works so well for layers of these dimensions. The three-band Kane model on which it is based is really only applicable over a limited energy range close to $\mathbf{k} = 0$ yet for the (4 + 4) sample the bottom of the electron subband is ~ 500 meV shifted from the GaAs conduction-band edge. Assuming that the structural integrity of the SL is maintained for the (2 + 2) sample examined in Ref. 13 then clearly by (2 + 2) the model has failed.

Drawing conclusions about the applicability of the simple decoupled model to the description of X-related transitions is a little more difficult, in part contributed to by the quite wide spread in experimental observations on samples which are nominally identical. This problem becomes particularly acute for SL dimensions of (4 + 4) and below. The combination of *our* X_z-Γ observations and the parameters we have chosen to use in the calculation persuades us that presently the limit of these calculation is at (8 + 8) [or possibly (6 + 6)] monolayers. However, this statement is not intended to be categorical and a number of factors should be borne in mind before considering this conclusion as absolute. Indeed, if we took *all* the data collected here we might conclude that the model works rather well even down to (3 + 3).

In our simple model, we assume that we are calculating the heavy-hole states correctly and therefore must be underestimating the position of the X-electron subbands in comparison to our observations. One possible reason for this could be an incorrect value of the X-electron wave vector in the GaAs. We have chosen to calculate its $\mathbf{k}$ vector using the band-edge value of the effective mass. The detailed band structure in bulk GaAs in the vicinity of the X points is complicated and a better model description should use some more appropriate approximation to the complex, nonparabolic dispersion. On an effective-mass sort of picture an improved dispersion would correspond to having a larger effective mass in the GaAs rather than the band-edge value of $1.3m_0$ that we have used in our rudimentary model. Intuitively, the consequence of this would be an enhancement of the subband energy. This is due to the faster decay of the wave function in the GaAs "barrier"—a situation tending toward the infinite well case where confinement energies would always be larger and bring the calculation more into line with our experimental observations.

One further thing to consider is our use of an idealized square-well potential for both the Γ- and X-related superlattices. In a recent publication Nelson, Miller Tu, and Sputz[37] have determined the binding energies of excitons in very thin GaAs-(Al,Ga)As quantum wells, where interruption of growth meant that the layer thicknesses were known to be in discrete monolayer steps. An envelope-function calculation was employed to determine accurately the lowest subband eigenvalues and a correction made to the eigenvalues based on the fact that the wells were not precisely square. Evidence for a transition of

the potential profile over a monolayer was claimed from the work of Van de Walle and Martin on the ideal, (001) GaAs-AlAs heterojunction.[38] Were such a grading of the potential profile present then it would, of course, alter the eigenvalues of the system we are considering, becoming an increasingly important effect as the superlattice dimensions become smaller. The net effect would be to increase the value of *all* the eigenvalues[39] of the system and qualitatively move the calculations toward our experimental observations.

As a general point, the spread in data for samples where $(n+m)\leq 8$ indicates the clear need for some improved structural characterization of similar samples, perhaps using Raman spectroscopy.[40] If the samples really have the dimensions that the authors suggest they have, then something is clearly questionable in the identification by each of the groups of their spectral features as being intrinsic.

CONCLUSIONS

A series of $(\mathrm{GaAs})_n$-$(\mathrm{AlAs})_m$, short-period SL's has been fabricated with $n=m=2,4$, 5, 6, and 8. Careful PL and PLE measurements have revealed that for $n=m\geq 4$ the lowest-lying conduction-band state is a folded X_z minimum and the SL's can be considered as "pseudodirect." For our samples the smallest energy gap does not approximate to that of the $Al_{0.5}Ga_{0.5}As$ alloy until the period is reduced to only 4 ML. A simple decoupled, Kronig-Penney-type model of the principal energy gaps in this system shows surprisingly good agreement with the observed direct, Γ-Γ transitions for samples with $m=n\geq 4$ ML. For our samples, favorable comparison of this simple model with measured X_z-Γ transitions presently breaks down below $n=m=6$. This is most likely due to an underestimate of the energy of the AlAs, X_z-subband minima and the use of an idealized square-well profile. Finally, cross comparison of many of the published spectroscopic data reveals the need for much more detailed *microscopic* information on the lateral structure of the sample on the scale of the exciting probe, i.e., exciton diameter, as compared to the "average" quantities yielded by the current x-ray analysis.

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