Evidence of type-I band offsets in strained $GaAs_{1-x}Sb_x/GaAs$ quantum wells from high-pressure photoluminescence

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We have used high-pressure photoluminescence in a diamond-anvil cell to investigate the band offsets between strained $GaAs_{1-x}Sb_x$ and unstrained GaAs for $x=0.12$. It has generally been expected that this system should display a strongly type-II band lineup, with holes confined in deep $GaAs_{1-x}Sb_x$ wells and the lowest-energy electron states in GaAs. Our results on a multiple-quantum-well sample show that this is not the case. We measure the photoluminescence transition energies up to and beyond the Γ-X crossover near 36 kbar, where the luminescence becomes indirect. The character of the Γ-X crossover dependence on well width requires a type-I offset for the X minimum and suggests a type-I offset for the Γ minimum of the conduction band. This is in good agreement with theory when the strong band-gap bowing in the $GaAs_{1-x}Sb_x$ alloy system is properly taken into account.

I. INTRODUCTION

There is at present considerable interest in strained-layer semiconductor systems both for their device potential, best illustrated by the $In_xGa_{1-x}As/In_xGa_{1-x}AsP$ strained-layer laser,[1] and for their novel physics, which is a consequence of the breaking of the cubic symmetry of the zinc-blende semiconductor structure.[2] A system which has much potential for scientific and practical interest is $GaAs_{1-x}Sb_x/GaAs$. It is known that the interface of GaSb and InAs has a broken band gap, the conduction-band edge of InAs having a lower electron energy than the valence-band edge of GaSb,[3] and it is also known that $GaAs_{1-x}Sb_x$ and $In_xGa_{1-x}As$ alloys with compositions close to GaAs have similar band gaps for the same lattice mismatch with respect to GaAs.[4,5] It may therefore be predicted that the $GaAs_{1-x}Sb_x/GaAs$ system will exhibit many of the interesting features of the $In_xGa_{1-x}As/GaAs$ system, but with a greater valence-band offset and a smaller conduction-band offset. An important stage in the understanding of this strained system is therefore to determine the offsets in the valence and conduction bands for the pseudomorphic heterojunction of $GaAs_{1-x}Sb_x$ on a GaAs substrate; this is the object of the present paper. We investigate a $GaAs_{1-x}Sb_x/GaAs$ multiple-quantum-well (MQW) system with $x=0.12$ and conclude that our results are best explained by a type-I band lineup, with both electrons and holes confined in the $GaAs_{1-x}Sb_x$ layers. This system has previously been investigated by Ji *et al.*,[6] who used photoreflectance techniques to study samples with $x=0.10$ and concluded that the band lineup was type II with the electrons in the GaAs barriers; our conclusions are therefore opposite to those from this previous study. We have previously given a brief account of our work,[7] and present a fuller report here.

We use a combination of photoluminescence (PL) at atmospheric pressure and high-pressure PL to investigate the sample. It is notoriously difficult to deduce accurate band offsets using only atmospheric pressure PL;[8] the additional information obtained by measuring PL peak energies as a function of hydrostatic pressure allows a more accurate determination of band offsets.[9] We measure the PL peak energies up to and beyond the conduction-band Γ-X crossover pressure, near 36 kbar, where the emissions change from being Γ_{8v}-Γ_{6c} direct transitions with a pressure coefficient of order 10 meV/kbar, to Γ_{8v}-X_c indirect transitions with a coefficient of order -2 meV/kbar. The dependence of the Γ-X crossover pressure and energy on well width can only be fitted by a small, but type-I offset, with electrons confined in the $GaAs_{1-x}Sb_x$ layers. A strongly type-II band structure is inconsistent with both the ambient-pressure PL data and the measured pressure dependence of the peak energies. (We assume throughout this paper that the holes are strongly confined in the $GaAs_{1-x}Sb_x$ layers—see Sec. IV B— so that type-I and type-II offsets refer to positive and negative conduction-band offsets, respectively.)

The sample whose PL properties are reported in this paper has been produced as part of a program of experimental work on strained $GaAs_{1-x}Sb_x/GaAs$ structures; its characterization is supported not only by the measurements which have been made on this sample and directly related calibration samples, but also by the general pattern of assessment and experimental work on a large number of structures with alloy concentrations ranging from 4% to 45%. The details of the growth and materials assessment are presented in Sec. II, while the PL data at atmospheric pressure and as a function of hydrostatic pressure are presented in Sec. III. The analysis and inter-

pretation of the results is given in Sec. IV. Finally, we summarize our results and conclusions in Sec. V.

II. EXPERIMENTAL DETAILS AND SAMPLE CHARACTERIZATION

The $GaAs_{1-x}Sb_x/GaAs$ structure considered here contained five epitaxial $GaAs_{1-x}Sb_x$ layers of different thicknesses separated by thick layers of GaAs. The sample was grown by molecular-beam epitaxy in a Riber 2300 growth chamber from elemental sources which give beams of Ga atoms, As_4 tetramers, and Sb_4 tetramers with a small proportion of Sb_2 dimers. The sample was grown on a GaAs substrate soldered to a molybdenum block with indium; the substrate temperature throughout growth was 550 °C as measured by an Ircon pyrometer sensitive only to the wavelength band in which GaAs is strongly absorbing at these temperatures. This growth temperature has been shown by transmission electron microscopy to give smooth heterointerfaces.[10] The As_4 and Ga fluxes were constant throughout the growth and the latter corresponded to a GaAs growth rate of 0.97 μm per hour. The alloy regions were grown by opening the shutter in front of the Sb cell for the time required to grow the appropriate thickness of $GaAs_{1-x}Sb_x$. The transient in the Sb flux following shutter operation had been observed previously with the monitor ion gauge and a compensating variation of the set point of the Sb cell temperature controller was derived. These changes in the set point on and after the operation of the Sb cell shutter were observed to give a constant Sb flux; they were used during the growth of each $GaAs_{1-x}Sb_x$ layer. The structure was grown on a semi-insulating GaAs substrate; a 0.5-μm GaAs buffer layer was followed by five successive $GaAs_{1-x}Sb_x$ layers which were grown for times calculated to produce widths of 83, 39, 28, 20, and 14 Å, respectively. The $GaAs_{1-x}Sb_x$ layers were separated from each other by 1000 Å of GaAs so that each quantum well would be isolated, both electronically and structurally, from its neighbors. The same thickness of GaAs was grown on top of the thinnest alloy layer.

The Sb concentration in the alloy layers was determined by the growth of a 5-μm layer of $GaAs_{1-x}Sb_x$ on a GaAs substrate with identical substrate temperature and source fluxes. The alloy concentration of this thick layer was found to be 12% by analyzing double crystal x-ray-diffraction rocking curves taken around the ⟨004⟩ peak on the assumption that the alloy layer was completely relaxed. This structure was used to calibrate a dynamic secondary-ion-mass-spectrometry (SIMS) system which was then used to analyze the structure studied in this paper. The limited depth resolution of the SIMS system broadens the Sb signal associated with each of the thin alloy layers and does not allow a direct measurement of the concentration profile in the sample. However, the integrated Sb signal for each of the alloy layers separately was found to be that expected for a 12% alloy concentration and a layer thickness equal to that calculated from the growth times.

Transmission-electron microscopy of the structure was carried out on a sample that had been thinned and was observed along the [110] pole. Dark field diffraction contrast images showed five layers of uniform contrast and thicknesses equal to those expected from the growth conditions within the accuracy (±7%) of the measurements. Lattice-imaging photographs of the individual layers are difficult to interpret: there is some contrast which varies across the sample in the area occupied by the alloy layers; this is believed to be due to strain and does not allow further quantitative information on the well thickness or uniformity to be obtained. No dislocations were observed within the structure.

The thick alloy calibration layer gave photoluminescence (PL) at 3.8 K with peak emission energy at 1.267 eV and a full width at half maximum (FWHM) of 25 meV. This is consistent with band-to-band luminescence for an Sb content of 12% if we take the band gap as

$$E_g(x) = 1.519\,14 - 1.908x + 1.2x^2 \text{ eV}$$
$$= 1.3075 \text{ eV} \quad (1)$$

from the values given for the binary band gaps at low temperature and the bowing parameter given for room temperature in Ref. 11. There remains a discrepancy of 40 meV; this is believed to be partly due to the Stokes shift expected for such a broad emission, and partly to the participation of shallow acceptors in the emission mechanism.

For the high-pressure PL measurements, the substrate was thinned mechanically to about 30 μm thick and the sample was cleaved to about 50×100 μm for loading, together with a piece of $In_{0.53}Ga_{0.47}As$ on InP to serve as the pressure gauge, in the diamond-anvil cell (DAC).[12] The $In_{0.53}Ga_{0.47}As$ has a known pressure coefficient of 10.9 meV/kbar (Ref. 13) and can be used to measure pressures up to 70 kbar. Argon was used as the pressure transmitting fluid. The PL spectra were obtained at 20 K, with pressure changes also being made at this temperature.

III. EXPERIMENTAL RESULTS

The photoluminescence from the MQW sample at 3.8 K is shown in Fig. 1. There are five strong, sharp PL

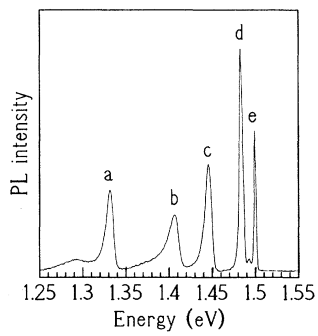

FIG. 1. Photoluminescence spectra of the $GaAs_{0.88}Sb_{0.12}/GaAs$ multiple-quantum-well sample at 3.8 K at ambient pressure. The sharp PL peaks are associated with the quantum wells which are of width (a) 83, (b) 39, (c) 28, (d) 20, and (e) 14 Å, respectively.

TABLE I. Measured energies, pressure coefficients, and crossovers.

Well width Å	Peak energy eV	dE_g^{Γ}/dP meV/kbar	dE_g^{X}/dP meV/kbar	Crossover pressure kbar	Crossover energy eV
GaAs	1.515[a]	10.7[b]	−1.43[b]	41.3[b]	1.951[b]
14	1.497				
20	1.482	10.4	−2.2	37.6	1.873
28	1.445	10.2	−2.3	36.9	1.821
39	1.406	10.0	−2.3	36.1	1.767
83	1.330	9.5	−2.2	35.1	1.664

[a]See Ref. 11.
[b]See Ref. 9.

emission lines, associated with recombination in each of the five quantum wells. The shoulder to the low-energy side of the emission of the two widest wells is associated with the wells, and is observed in other samples including single quantum-well samples. The FWHM of the quantum-well emissions are 9 meV (83 Å), 13 meV (39 Å), 9 meV (28 Å), 4 meV (20 Å), and 2.5 meV (14 Å), respectively. The intensities of the MQW PL signals are consistent with quantum wells of type-I structure, with both electrons and holes confined within the alloy layers, as a much weaker PL signal is generally found from type-II quantum wells.

The variation in PL peak energy with hydrostatic pressure is shown in Fig. 2 for the quantum wells of width between 20 and 83 Å. The PL from the 14-Å well disappears by 6 kbar, and is not plotted in Fig. 2. Two features are of particular note in Fig. 2. First, the emissions cross over from being Γ-Γ direct transitions, with a pressure coefficient near 10 meV/kbar, to Γ-X indirect transitions, with a coefficient near −2 meV/kbar, between 35.1 and 37.6 kbar (Table I). These pressures are below the GaAs Γ-X crossover pressure of 41.3 kbar,[9]

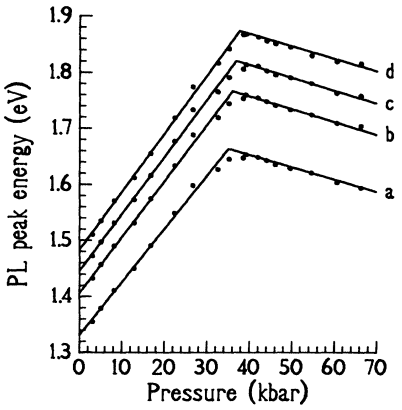

FIG. 2. Variation of PL peak energies as a function of hydrostatic pressure for the $GaAs_{0.88}Sb_{0.12}$ quantum wells of width (a) 83, (b) 39, (c) 28, and (d) 20 Å, respectively. The transitions cross over around 36 kbar from Γ-Γ direct transitions, with pressure coefficients near 10 meV/kbar, to Γ-X indirect transitions, with pressure coefficients near −2 meV/kbar. Below crossover, the pressure coefficients vary from 9.5 meV/kbar for the 83-Å well to 10.4 meV/kbar for the 20-Å well.

and so the $GaAs_{0.88}Sb_{0.12}$ X states must lie below the GaAs X states. Second, the pressure coefficient of the Γ-Γ transitions between 0 and 36 kbar decreases with increasing well width, from 10.4 meV/kbar in the 20-Å well to 9.5 meV/kbar in the 83-Å well (Table I). The pressure coefficient for each narrow well was obtained by plotting the *difference* between the PL energy of that well and of the widest well as a function of the wide-well emission energy. The relative accuracy of the PL pressure coefficients listed in Table I is therefore better than ±0.1 meV/kbar,[14] as the error in the relative emission energies at a given pressure is much smaller than the error in measured pressure. The variation of pressure coefficient with well width is surprisingly large and the magnitude of the wide-well value is surprisingly low: the Γ-Γ gap increases at 10.7 meV/kbar in GaAs (Ref. 9) and in GaSb coefficients of 14.5 meV/kbar (Ref. 15) and 13.8 meV (Ref. 16) have been reported. Linear interpolation gives an expected pressure coefficient of 11.2 meV/kbar in the wide $GaAs_{0.88}Sb_{0.12}$ wells. However, anomalously low pressure coefficients appear to be characteristic of strained layers in the III-V alloys: they have also been observed in strained $In_xGa_{1-x}As$ type-I quantum wells between unstrained GaAs barriers,[14,17–19] and we have also observed them in strained $In_xGa_{1-x}As_yP_{1-y}$ wells in unstrained InP barriers (to be reported elsewhere). The anomalously low values are at present unexplained, but this is not our present concern. We shall instead use the data in Figs. 1 and 2 to deduce the band-offset ratio between strained $GaAs_{0.88}Sb_{0.12}$ and unstrained GaAs.

IV. ANALYSIS

In this section, we consider what models of the heterostructure band structure are qualitatively consistent with the data, and we find that only a type-I model with a small conduction-band offset can account for all the results.

A. Photoluminescence peak energies

All that can be deduced from the ambient-pressure low-temperature PL peak energies is that the system cannot be strongly type II. The quantum wells, at 12% Sb content, are under a biaxial compressive strain of 0.0087. The hydrostatic component increases the Γ_6-Γ_8 band gap

(mostly by raising the conduction-band Γ_6 state) by about 74 meV. The shear component splits the valence band, bringing the heavy-hole states up by about 29 meV (decreasing the band gap). Thus the predicted strained band gap is 1.353 eV. However, using the experimentally determined unstrained band gap of 1.267 eV in the calibration layer and including the corrections for strain, we obtain 1.312 eV for the strained band gap. For this range of band gap, 1.312–1.353 eV, the sum of the offsets, $\Delta E_v + \Delta E_c$, lies between 206 and 168 meV. The photoluminescence energies from type-I quantum wells are then expected to range between a minimum of 1.312 eV, for very wide wells, and the GaAs band-gap energy in the limit of very narrow wells. We calculate the confined-state energies using the envelope-function method, assuming parabolic bands, and taking the electron effective mass m_Γ^* to be 0.0665 in GaAs and 0.063 in $GaAs_{0.88}Sb_{0.12}$, by linear interpolation between the GaAs and GaSb values. We assume the heavy-hole effective mass along the growth direction, m_h^*, to be given by the GaAs value[20] $m_h^* = 0.35$ in both the alloy wells and GaAs barriers. The GaAs band gap is 1.519 eV. The predicted PL energy is plotted in Fig. 3 as a function of well width, for various type-I band-offset ratios. Because of the uncertainty in the strained band gap, we use it as a fitting parameter for Fig. 3. We see that the narrower wells are not very sensitive to the band-offset ratio, because the energies are in any case close to the barrier band gap. This is consistent with both type-I and type-II configurations. The widest well, however, has little hole confinement energy $E_{\rm con}^v$, and so its emission energy is given for both type-I and type-II configurations by

$$\begin{aligned} E_{\rm PL} &= E_g^{\rm alloy} + E_{\rm con}^c \quad \text{type I} \\ &= E_g^{\rm alloy} - \Delta E_c \quad \text{type II} . \end{aligned} \tag{2}$$

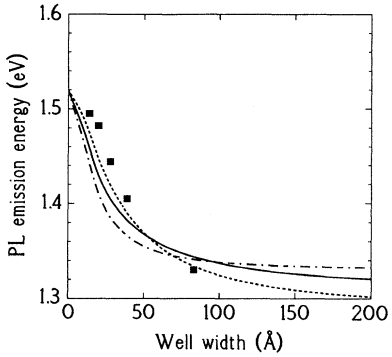

FIG. 3. The data points show the PL peak emission energies as a function of well width at ambient pressure. The theoretical curves show the best fits to the experimental data obtained using a type-I model, with conduction-band to valence-band offset ratios ΔE_c:ΔE_v of 0:100 (dot-dashed line), 25:75 (solid line), and 50:50 (dashed line). The strained-alloy band gap has been varied as a free-fitting parameter. For a band-offset ratio of 0:100 the best fit to the data is obtained for a band gap of 1.33 eV, while for a 50:50 offset ratio a reasonable fit requires the band gap to be decreased to 1.26 eV.

In fact, its energy is 1.335 eV, within the expected range of band gap for the strained 12% alloy, 1.312–1.353 eV. A significant type-II conduction-band offset ΔE_c, from Eq. (2), would have to be compensated for by increasing the strained $GaAs_{1-x}Sb_x$ band gap, requiring a reduction of the Sb content in the wells. Since the strained band gap decreases at about 16 meV for each percent of Sb, a type-II offset of, for example, 100 meV, would require the Sb content to be reduced by 6%—halved—to account for the emission energy of the widest well. Consequently, we conclude that the GaAs/$GaAs_{1-x}Sb_x$ system is not strongly type II.

In contrast, the peak energies of the narrower wells are difficult to interpret. For infinitely narrow wells, in any model, the emission energy goes to that of the barrier material. As seen in Fig. 3, the narrower wells give consistently higher emission energies than either model, whether type I or II. It is not clear why this is so. There are so many uncertain parameters—including well width and composition, and the well shape if interdiffusion or segregation occur—that a detailed theoretical analysis is not likely to be fruitful. However, the pressure dependence of the luminescence does display, as we shall see, certain features that allow conclusions to be drawn independently of these uncertainties.

B. Γ-*X* crossover pressures and energies

The high-pressure crossover can be identified as a Γ_6^c-X^c crossover from the characteristic pressure coefficients below crossover (~10 meV/kbar) and above (~−2 meV/kbar). It shows three features of crucial importance to the interpretation. First, in all the wells, it occurs at *pressures* below the known GaAs Γ-*X* crossover. Secondly, it occurs at *energies* below the known GaAs Γ-*X* crossover. And, third, it occurs at *lower* pressures in *wider* wells. The first feature requires that the crossover be with the *X* states in the wells, not the barriers. The second point requires that the well *X* minima be some 100 meV below the barrier *X* minimum (see below). And the third feature requires that the electron energies in the various Γ_c wells are not very different. This requires that the Γ_6 band lineup is close to the type-I–type-II borderline, and confirms our assumption that the holes are strongly confined in the $GaAs_{1-x}Sb_x$ layers.

A priori, there are several possible crossovers. If the Γ_6 band lineup is type II, the relevant electron level for crossover is the GaAs conduction-band edge, while if it is type I the electrons are confined in the wells. The *X* states may be those of the barrier or they may be the well $X_{x,y}$ states, brought down by the strain-induced splitting of the $GaAs_{1-x}Sb_x$ *X* minima. The GaAs Γ-*X* crossing is well known. It occurs at about 41 kbar,[9] and in our samples would be independent of well width. On both counts the crossing we observe cannot be this, and so the electron cannot be in the barriers.

If the conduction-band Γ offset is type I but the confined electron states in the well cross against the GaAs *X* levels, more than 41 kbar would be required to reach crossover. Also, the higher-energy electrons in the

narrower wells would cross first. Both points are contrary to the data. We are left with well (type-I) or barrier (type-II) electrons crossing against the well $X_{x,y}$ levels. This will happen if the combination of band-offset ratio and strain-induced splitting can bring the well $X_{x,y}$ levels below the barrier X. Evidently, this is easier if the Γ offset ratio is type I rather than type II, so as to keep the entire band structure of the wells low relative to that of the barriers, and it is not possible if the system is strongly type II.

The different pressures at which crossover occurs in the different wells correspond to an increase in the energy of the X electrons in the narrower wells. Furthermore, the X-electron energy must increase faster with decreasing well width than the Γ-electron energy. Clearly, this presents no difficulty for a type-II model, in which the relevant electrons are all at the edge of the barrier conduction band. For a type-I model it requires that the system is only weakly type I, so that the Γ_{6c}-electron energies change only a little with well width, less than the $X_{x,y}$ electrons. We have seen above that we do not predict accurately the energy of the narrower wells, but whatever the reason for the Γ and X energy changes, whether well shape, composition, or simply confinement energy, this constraint implies that the system is not strongly type I.

We now consider the crossover energies. The 20-Å well emits at an energy very close to the barrier band gap, only 40 meV below, and so its holes cannot be more than 40 meV above the barrier valence-band edge, whether the electrons are type I or II. Nevertheless, the crossover for this well occurs at 1.87 eV, compared with the value of 1.95 eV in GaAs.[9] Thus the lowest confined X level must be at least 40 meV below the GaAs X minimum. Then the crossover for the widest well occurs at 2.5 kbar lower pressure, which requires its lowest X level to be at least another 25 meV lower in energy. However, the Γ_{6c}-X_c splittings in GaAs and GaSb are very similar, 460 and 430 meV, respectively. There are no data for the bowing of the indirect gap, but it is likely to be less than the large bowing of the direct gap in this alloy as it is in most of the ternary alloys in which it has been measured. Consequently, if the Γ conduction band is flat (zero offset) across the heterojunction, the average X minimum is expected to be flat as well, or even be type II, rising in the well. The axial strain splits the X minima by about 50 meV, and this is not sufficient to account for the >65 meV depth of the X well. Thus the whole of the band structure of the $GaAs_{1-x}Sb_x$ must be shifted down from a flat conduction band, and so the system is type I.

C. Pressure coefficients

The pressure coefficients of the quantum wells are consistent with this conclusion. As remarked above, they are anomalously low, and this is characteristic of type-I strained quantum wells. If the system was type II with the electrons in the GaAs, the pressure coefficient would be that of the GaAs band gap, 10.7 meV/kbar, modified slightly by the pressure coefficient of the valence-band offset and the change in hole confinement energy with pressure. These corrections are not expected to be as large as the -1.2 meV/kbar required to give the observed value of 9.5 meV/kbar for the widest well. The same, of course, would apply if the system were type II with the holes in the GaAs, *mutatis mutandis*.

V. DISCUSSION AND CONCLUSIONS

Our conclusion that the band offset between strained $GaAs_{0.88}Sb_{0.12}$ and unstrained GaAs is type I is contrary to previous expectations. Ji *et al.*[6] studied strained-layer $GaAs_{0.9}Sb_{0.1}$/GaAs MQW's using photoreflectance and concluded that the band lineup was type II, with the valence-band offset ΔE_v being 1.7 times the difference in band gaps, ΔE_g. We note, however, that their data included a number of unexplained features and that some of the higher-lying features in particular were not well fitted by their model. Further, our data cannot possibly be interpreted by such a large type-II offset, which makes the X minima type II also and would give Γ-X crossover at 41 kbar and 1.95 eV for all well widths.

Our results are consistent with the band offsets predicted by the model-solid theory of van de Walle,[21] when the strong band gap bowing in this alloy system[5,10] is taken into account. Using the model-solid theory, we do indeed calculate a type-II lineup when strained GaSb is grown on GaAs, with holes confined in a GaSb well which is 1039 meV deep, and electrons seeing a GaSb barrier of 588 meV. The model-solid theory is based on the local-density-functional pseudopotential method, whose best-known deficiency is its failure to produce the correct band gap. The model-solid theory is therefore applied by calculating the valence-band offsets between the two semiconductors under consideration and then adding to each material its respective band gap to deduce the conduction-band offset. When this procedure is applied to the strained $GaAs_{0.88}Sb_{0.12}$/unstrained GaAs heterojunction, we obtain a valence-band well of 131 meV in $GaAs_{0.88}Sb_{0.12}$ and, using the theoretically estimated strained-alloy band gap of 1353 meV, the conduction-band well is in $GaAs_{0.88}Sb_{0.12}$, and is 35 meV deep—type I, in agreement with our conclusions.

We do not believe that the band offsets can be determined quantitatively from the samples and experiments described here. The situation is the same as in the $In_xGa_{1-x}As$/GaAs system[14] and the $In_xGa_{1-x}Sb$/GaSb system:[16] because the Γ-X crossover occurs between the quantum well Γ_c and the quantum well X_c states, rather than the barrier X_c states, it does not give an accurate spectroscopic determination of the band-offset ratio. While in principal it could be determined from fitting to the data, the uncertainties lead to large errors as in the case of fitting to the PL peak energies.[8] The best one can do with these structures is to put limits on the band offsets according to qualitative features of the PL and its pressure dependence, as we have done here. A quantitative determination awaits samples in which crossover is known to occur against the barrier states; these can be achieved by adding aluminum to the barriers to lower the barrier X minimum. We have shown that high-pressure

experiments on $In_xGa_{1-x}As/Al_yGa_{1-y}As$ samples yield the $In_xGa_{1-x}As/GaAs$ band offsets,[22] and the method should be applicable to suitable $GaAs_{1-x}Sb_x/Al_yGa_{1-y}As$ structures.

In summary, we have used high-pressure photoluminescence in a diamond-anvil cell to determine the band offsets between strained $GaAs_{1-x}Sb_x$ and unstrained GaAs for $x=0.12$. We first considered the ambient-pressure photoluminescence peak energies from which we drew the weak conclusion that the system cannot be strongly type II. We measured the photoluminescence transition energies up to and beyond the Γ-X crossover near 36 kbar, where the luminescence became indirect. The Γ-X crossover pressures are lower than the GaAs value of 41 kbar, and this requires that the X states have a type-I lineup. Combining this result with the crossover energies, we conclude that the Γ states have a weakly type-I lineup. The variation of pressure coefficient with well width is consistent with this result. The band-offset ratio will change rapidly with alloy composition x in this system, because of the strong band-gap bowing of the alloy. Our results are in good agreement with theory when this band-gap bowing is taken into account.

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