Pressure dependence of band offsets in $InAs/Ga_{1-x}In_xSb$ superlattices

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(Received 3 April 1996; revised manuscript received 22 October 1996)

We have determined the pressure dependence of the valence-band offset between InAs and $Ga_{1-x}In_xSb$ ($x\sim0.25$) by measuring the midinfrared photoluminescence (PL) of two $InAs/Ga_{1-x}In_xSb$ superlattice samples at liquid nitrogen temperature under hydrostatic pressures up to 40 kbar. The PL peaks move to higher energy with pressure at rates of 8.3 ± 0.1 and 8.8 ± 0.3 meV/kbar for the two samples. By comparing these results with a calculation based on the envelope function formalism, we deduced the pressure dependences of the valence-band offset between InAs and $Ga_{1-x}In_xSb$ of these samples to be 3.5 ± 1.6 and 5.6 ± 2.5 meV/kbar, respectively. These values are compared with the results of transport measurements on $InAs/Ga_{1-x}In_xSb$ ($x\leq0.1$) as well as a theoretical prediction for InAs/GaSb based on the model solid theory.
[S0163-1829(97)02907-X]

I. INTRODUCTION

The $InAs/Ga_{1-x}In_xSb$ heterostructure system possesses a broken-gap type-II band alignment: the conduction-band minimum of InAs, E_c^{InAs}, lies below the valence-band maximum of $Ga_{1-x}In_xSb$, $E_v^{Ga_{1-x}In_xSb}$. The band overlap Δ, equal to $E_v^{Ga_{1-x}In_xSb}-E_c^{InAs}$ may also be equated to $\Lambda-E_g^{InAs}$, where E_g^{InAs} is the band-gap energy of InAs, and Λ is the offset between the valence bands of InAs and $Ga_{1-x}In_xSb$. Because of this unusual band lineup, the electronic properties of the heterostructure are strongly dependent on the precise magnitudes of Λ and Δ. This applies especially to the effect of pressure on transport properties, while, by the same token, the pressure effects provide a sensitive test of asserted band alignments.

The values reported in the literature for the pressure dependence of the band overlap Δ for $InAs/Ga_{1-x}In_xSb$ heterostructures with $x\leq0.1$ vary significantly, ranging from -12 to -5.8 meV/kbar.[1–6] If one accepts the literature value for dE_g^{InAs}/dP of 10 meV/kbar,[7] this corresponds to a pressure dependence of the valence-band offset Λ of -2 to $+4.2$ meV/kbar. In most cases,[2–6] the pressure dependence of Δ is estimated by modeling the measured pressure dependence of the carrier densities, and the large variation in the resultant $d\Delta/dP$ and $d\Lambda/dP$ values is believed to be caused by different extrinsic charge densities in the samples measured.[3] There have been few optical measurements since the magneto-optical studies of Claessen *et al.*,[1] apparently because of the relatively poor radiative efficiencies of these samples. Recent progress in the sample growth technique,[8,9] as shown by the observation of stimulated emission,[9] has made it possible to obtain high-optical-efficiency $InAs/Ga_{1-x}In_xSb$ superlattices as previously predicted for $x\approx0.25$,[10,11] allowing photoluminescence (PL) measurements under high hydrostatic pressure. The advantages of the PL measurements over the transport measurements are (1) the insensitivity of the PL peak energy to the extrinsic charge densities, and (2) the higher accuracy in determining the pressure shift of the band-gap energy owing to the narrow PL peaks (with respect to the pressure shift of the peaks). In this paper, we report the determination of the pressure dependence of the valence-band offset in $InAs/Ga_{1-x}In_xSb$ superlattices from measurements of the PL at 80 K on two samples with $x=0.25$ and 0.31.

II. EXPERIMENT

Two samples were grown on GaSb substrates by molecular-beam epitaxy, as described elsewhere.[9] The samples were grown to be nominally four periods of 35-Å/16.7-Å $Ga_{0.75}In_{0.25}Sb/InAs$ superlattices with an additional layer of $Ga_{0.75}In_{0.25}Sb$. The growth was interrupted for 5 s at each interface of the superlattices under a Sb flux, in order to force InSb-like interfaces. After the growth, the actual layer thicknesses and compositions were estimated by x-ray-diffraction measurements: 38-Å/19-Å $Ga_{0.69}In_{0.31}Sb/InAs$ for sample *A*, and 35-Å/15-Å $Ga_{0.75}In_{0.25}Sb/InAs$ for sample *B*.

For pressure measurements, the samples were thinned down by lapping and polishing the GaSb substrates to thicknesses of ~50 μm, and then were cleaved to dimensions of $\sim180\times180$ μm^2. A cleaved piece of a sample was loaded into an NBS-type diamond-anvil cell (DAC) (Ref. 12) with a type-IIa diamond anvil or a sapphire ball cell (SBC),[13] along with $\sim$20-μm ruby chips for pressure calibration. As a pressure medium we used a 4:1 mixture of methanol:ethanol, which has been shown to give hydrostatic pressures in cryogenic experiments if the pressure is changed at room temperature.[14] The cells were mounted in a liquid-nitrogen

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cold-finger Dewar. The 5145-Å line of an argon-ion laser, modulated by an optical chopper at 800 Hz and focused to a beam diameter of $\sim 100\ \mu$m with a power density of 2×10^2 W/cm^2 at the sample, was used as excitation radiation. The luminescence was dispersed by a Jarrell-Ash half-meter grating monochromator (resolution ~ 2 meV) and detected by an Infrared Associates mercury-cadmium-telluride detector cooled with liquid nitrogen. A Ge($\lesssim$ 600 meV) or Si ($\gtrsim$ 600 meV) crystal was used to prevent scattered laser light and/or the PL from the substrate from entering the monochromator. A magnified image of the pressure compartment was projected onto a screen *in situ* to monitor the focusing of the laser beam on the sample or on the ruby chips. The detector signal was processed using a preamplifier and a lock-in amplifier and recorded by a computer. For each luminescence measurement the pressure was changed at room temperature, and the value determined at 80 K using the pressure shift of the ruby $R1$ luminescence line for experiments in the DAC, and the PL from the GaSb substrate for those in the SBC, where luminescence from sapphire interfered with the ruby luminescence.

III. RESULTS

Figures 1(a) and 1(b) show PL spectra of samples A and B, respectively, in the DAC at 80 K under pressure. The PL peaks move to higher energy with pressure with small changes in the widths. Figure 2(a) and 2(b) are plots of the PL peak energy vs pressure for these samples at pressures up to 40 kbar. Some data were taken after the pressure was increased from the previous data point, and others after reducing the pressure. No hysteresis is seen. Figure 2(a) is a collection of data from measurements of three pieces of sample A: (1) before thinning at zero pressure; (2) in the SBC at pressures between 0 and 7 kbar; and (3) in the DAC at pressures $\geqslant$24 kbar. Only one piece of sample B was measured. The PL peak energy could not be determined reliably in the range of 350–480 meV due to an atmospheric absorption band. In addition to this band, an absorption band of diamond in the range of 240–450 meV made it impractical to use the DAC for this range. The useful pressure range of the measurements in the SBC was limited by the change of the band gap of GaSb from direct (Γ-Γ) to indirect (Γ-L) near 7 kbar, beyond which the PL from the substrate, used for pressure calibration, becomes undetectable. The solid lines in Fig. 2 indicate the linear least-squares fits, giving a pressure coefficient of 8.3 ± 0.1 and 8.8 ± 0.3 meV/kbar for samples A and B, respectively.

The calculation of the pressure dependence of the band-gap energy should include the effect of the strain due to the dissimilar lattice constants of the substrate and superlattice layers. The substrate's lattice constant decreases under applied pressure according to the bulk modulus B,

$$a^{(s)}(P)=\left(1-\frac{P}{3B}\right)a^{(s)}(0). \tag{1}$$

The superlattice epilayers' lattice constant parallel to the interface is fixed to the substrate, and thus to be $a^{(s)}(P)$. The strain parallel to the interface,

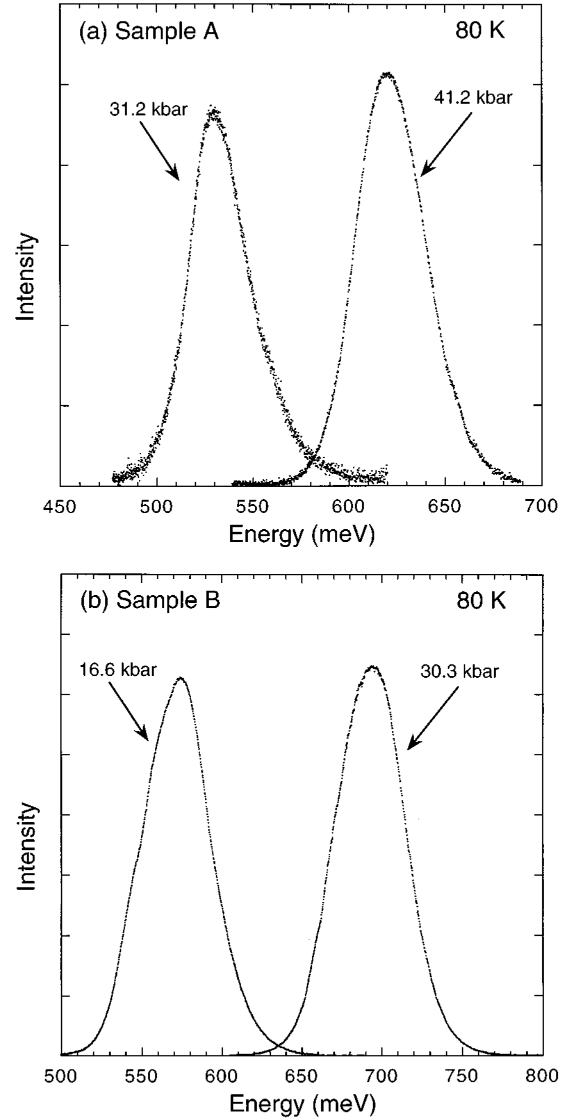

FIG. 1. Photoluminescence (PL) spectra of the samples under pressure in the DAC at 80 K. The PL peak shifts to higher energy with pressure with little change in the shape.

$$e_{\parallel}^{i}=\frac{a^{(s)}(P)-a^{i}(0)}{a^{(s)}(P)}, \tag{2}$$

differs for the two superlattice layers labeled by i. The strain in the growth direction, e_{zz}^{i}, is fixed by $e_{\parallel}^{i}$ and the applied pressure P according to Hooke's law:

$$-P=c_{11}^{i}e_{zz}^{i}+2c_{12}^{i}e_{\parallel}^{i}, \quad e_{zz}^{i}=-\frac{2c_{12}^{i}e_{\parallel}^{i}}{c_{11}^{i}}-\frac{P}{c_{11}^{i}}, \tag{3}$$

where c_{11} and c_{12} are elastic constants. The hydrostatic strain

$$e_{H}^{i}=2e_{\parallel}^{i}+e_{zz}^{i}=\left(2-\frac{2c_{12}^{i}}{c_{11}^{i}}\right)e_{\parallel}^{i}-\frac{P}{c_{11}^{i}}, \tag{4}$$

and the biaxial strain

$$e_{B}^{i}=e_{\parallel}^{i}-e_{zz}^{i}=\left(1+\frac{2c_{12}^{i}}{c_{11}^{i}}\right)e_{\parallel}^{i}+\frac{P}{c_{11}^{i}} \tag{5}$$

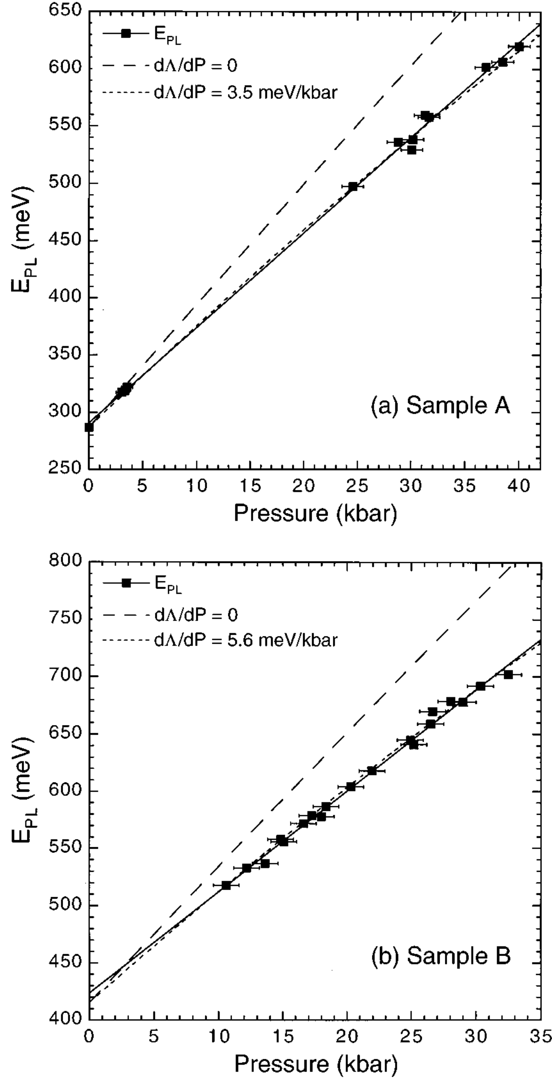

FIG. 2. Pressure dependence of the PL peak energies. The solid lines indicate the linear least-squares fits. The other curves indicate the calculated pressure shift of the band gaps for various assumed values for the pressure dependence $d\Lambda/dP$ of the valence-band offset.

are then used to describe the effect of strain on the band structure of the superlattice.

The pressure dependence of the band gaps of these samples has been calculated using an envelope-function approximation and a multiband effective-mass Hamiltonian. The Hamiltonian is obtained by describing the bulk with a modified eight-band Kane model using empirical parameters.[15,16] Parameters for $InAs/Ga_{1-x}In_xSb$ superlattices are shown in Table I. The valence-band offset is chosen for the best fit to the fundamental gaps measured in Ref. 8. The layer thicknesses were adjusted to 37.2 Å/19.8 Å and 36.9 Å/13.1 Å for samples A and B, respectively, to obtain the best fit with the data. Strain is accommodated within this formalism by shifting the zone-center energies of the bulk constituents according to deformation potentials c (hydrostatic) and b (biaxial):

$$E_C^i \rightarrow E_C^i + e_H^i c^i, \tag{6}$$

$$E_{\mathrm{HH}}^i \rightarrow E_{\mathrm{HH}}^i + e_B^i b^i, \tag{7}$$

$$E_{\mathrm{LH}}^i \rightarrow E_{\mathrm{LH}}^i - e_B^i b^i + 2(e_B^i b^i)^2/(E_{\mathrm{LH}}^i - E_{\mathrm{SO}}^i), \tag{8}$$

$$E_{\mathrm{SO}}^i \rightarrow E_{\mathrm{SO}}^i - 2(e_B^i b^i)^2/(E_{\mathrm{LH}}^i - E_{\mathrm{SO}}^i), \tag{9}$$

where C, HH, LH, and SO label the conduction heavy-hole, light-hole, and spin-orbit split-off bands, respectively. The deformation potential c parametrizes the shift of the conduction band relative to the valence band, whereas b parametrizes the heavy-hole–light-hole splitting in the valence bands.

The pressure dependence of the energy gap $E_g(P)$ was calculated for various assumed values of $d\Lambda/dP$. The results are shown in Fig. 2. For a given value of $d\Lambda/dP$, the calculated $E_g(P)$ shows a slightly sublinear pressure dependence. A calculation with $d\Lambda/dP=0$ gives $E_g(P)$ substantially different from the observed shift of the PL peak. Calculations with $d\Lambda/dP=3.5$ and 5.6 meV/kbar provide the best fits for samples A and B, respectively. The result for sample A is more reliable because the zero-pressure energy gap datum is particularly accurate due to a lack of uncertainty in the pressure; the uncertainty in $d\Lambda/dP$ due to the scatter in the data of this sample is ± 0.1 meV/kbar, while the uncertainty for sample B is ± 1 meV/kbar. From these estimates, it appears that $d\Lambda/dP$ may be different for the two samples.

IV. DISCUSSION

The uncertainty in the estimated values of $d\Lambda/dP$ consists of two parts: (1) experimental uncertainty due to the scatter in the data (± 0.1 and 1 meV/kbar for the two samples) and (2) error introduced in the calculation due to the limited knowledge of the input parameters for the calculation. The first is statistical, while the second is systematic and can be reduced if better values of the input parameters are known.

The primary source of uncertainty in the calculation is the uncertainty in the literature value of the hydrostatic deformation potential of InAs,c^{InAs}. A conservative estimate of this uncertainty in c^{InAs} would be about 0.5 eV. The hydrostatic strain resulting from the applied pressure mainly affects the conduction-band edge, and the conduction states reside mostly in the InAs layer. In contrast, the biaxial strain, which affects the heavy-hole energy, changes by less than 1% from 0 to 40 kbar, due to similar elastic constants in the substrate and epilayer. This change produces only a 0.1-meV/kbar change in the valence-band offset. A change in c^{InAs} of 0.5 eV would result in a change in $d\Lambda/dP$ of about 1.5 meV/kbar. The hydrostatic deformation potential is the only quantity where a change significantly affects $d\Lambda/dP$ *and* produces very little effect on the zero-pressure gap; for a change in c^{InAs} of 0.5 eV, the zero-pressure gap changes only 4 meV. The zero-pressure gap is far more sensitive to changes in layer widths or alloy compositions. An increase in the indium fraction of 6% increases $d\Lambda/dP$ by 0.3 meV/kbar, but also decreases $E_g(0)$ by 25 meV. A shift of 1.5 Å from the alloy layer to the InAs layer decreases $d\Lambda/dP$ by 0.8 meV/bar, but also decreases $E_g(0)$ by 30 meV. We thus estimate the systematic uncertainty in the calculation of

TABLE I. A summary of parameters used in the present calculations. The values are taken from Ref. 19, unless otherwise noted. For the parameters whose values at 80 K are not available, the values were estimated from the values for 4.2 K. The valence-band offset is chosen for the best agreement with the band gaps in Ref. 8. For the alloy layers, the lattice constant, deformation potentials, elastic constants, and spin-orbit splitting are linearly interpolated between the binary constituents. E_P, the energy associated with the momentum matrix element of the Kane model, is obtained from the conduction-band effective mass m_e, taken from Ref. 19, according to the equation $E_P=3E_g(E_g+\Delta)m_0/[m_e(3E_g+2\Delta)]$, where m_0 is the electron free mass. An average E_P is used for the superlattice.

	$Ga_{0.75}In_{0.25}Sb$	$Ga_{0.69}In_{0.31}Sb$	InAs
a lattice constant (Å)	6.192	6.215	6.058
b biaxial deformation potential (eV)	−1.85	−1.86	−1.8
c hydrostatic deformation potential (eV)	−8.15	−8.11	−5.8[a]
c_{11} (10^{11} dyn cm^{-2})	8.355	8.240	8.33
c_{12} (10^{11} dyn cm^{-2})	3.96	3.95	4.53
Δ spin-orbit splitting (eV)	0.769	0.772	0.380
E_g energy gap (eV)	0.581	0.536	0.41
m^*_{hh} in (100) direction	0.35[b]	0.35[b]	0.4[b]
$E_P=2\langle S\|p_z\|Z\rangle^2/m$ (eV)		22.8	
valence-band offset (meV)		560[c]	

[a]Reference 7.

[b]G. Bastard, Acta Electronica **25**, 147 (1983).

[c]This value is the valence-band offset for the unstrained system; the effect of strain is to split the top of the valence band, and as a result, the band offsets for the heavy and light holes are different. For example, for $x=0.25$, the heavy-hole offset is 640 meV, and the light-hole offset 486 meV. Λ in the text, on the other hand, refers to the actual offset between the valence-band maxima (the heavy hole of $Ga_{1-x}In_xSb$ and the light hole of InAs) (Ref. 10).

$d\Lambda/dP$ to be ± 1.5 meV/kbar. It should be pointed out, however, that this error is a systematic one for all samples, and it does not account for the difference in the $d\Lambda/dP$ of the two samples.

From these error estimates, we obtain $d\Lambda/dP=3.5\pm 1.6$ meV/kbar for sample A and $d\Lambda/dP=5.6\pm 2.5$ meV/kbar. Before we compare our result with the previous results, we should note that our analysis assumes that Λ is linearly dependent on pressure. If the dependence is nonlinear, our numbers represent the *average* values of $d\Lambda/dP$ for the pressure ranges used. For example, the four lowest pressure (0–4 kbar) data points in Fig. 2(a) give 9.9 ± 2.5 meV/kbar for the pressure coefficient of the PL energy, which in turn gives $d\Lambda/dP=1.7\pm 4.0$ meV/kbar. This suggests that the dependence of Λ on pressure could be nonlinear, although a definitive conclusion cannot be drawn due to the large error bars for the number for the low-pressure range. This could explain the difference between the results for the two samples; if data for sample B at low pressures were available, the average $d\Lambda/dP$ could be smaller than 5.6 meV/kbar.

Van de Walle[17] used the model-solid theory to calculate $d\Delta/dP$ for InAs/GaSb, and predicted -10.1 ± 3 meV/kbar, which is equivalent to $d\Lambda/dP=-0.1\pm 3$ meV/kbar if we use $dE_g^{InAs}/dP=10$ meV/kbar. This value of $d\Lambda/dP$ is quite different from our values of 3.5 ± 1.6 and 5.6 ± 2.5 meV/kbar, but well within the error bars of our low-pressure value from the discussion above. This agreement with the low-pressure value is intriguing when one considers the fact that his calculation of $d\Delta/dP$ is in the linear regime (low-pressure range).[18] This suggests a nonlinear pressure dependence of Λ. However, given the large error bars, this agreement could be fortuitous. We should also point out that the theoretical value for $d\Lambda/dP$ and our value for sample A for the whole pressure range are still within the error bars of each other.

Our values for $d\Lambda/dP$ are compared with the previous results in Table II. Our values are different from those from some transport measurements[3,5,6] which give $d\Lambda/dP\sim 0$, but are more in line with the values from magneto-optical measurements by Claessen *et al.*[1] and other transport measurements.[2,4] Given the disagreement among the results from transport measurements, the agreement with the only previous optical measurement by Claessen *et al.* is more meaningful than the disagreement with some of the transport results. It should be noted here that the samples in the previous measurements had alloy concentrations in the

TABLE II. Comparison of $d\Lambda/dP$ values for $InAs/Ga_{1-x}In_xSb$. All values, except for those from this work, are deduced from $d\Delta/dP$ using $dE_g^{InAs}/dP=10$ meV/kbar.

	Type of measurement	x	$d\Lambda/dP$
This Work	PL	0.31	3.5±1.6
		0.25	5.6±2.5
Ref. 1	Magneto-optical	0	4.2
Ref. 2	Magnetotransport	0	3.3
Ref. 3	Magnetotransport	0	0.1±1.0
Ref. 4	Magnetotransport	0	2.5
Ref. 5	Magnetotransport	0	0.5
		0.1	−2.0, 0.4
Ref. 6	Magnetotransport	0	0
Ref. 17	Theory	0	−0.1±3.0

$Ga_{1-x}In_xSb$ layers of $x=0$ or 0.1, while our samples have $x=0.31$ and 0.25. It is possible that $d\Lambda/dP$ is dependent on x, in which case the comparison with the previous results would not be significant, although comparison of our result with that of Claessen *et al.* suggests the contrary. In any event, our result is the only value for superlattices with $x\sim0.25$, which are technologically more important for mid-infrared light emitters and long-wavelength infrared detectors than those with $x\sim0$.

In summary, we have measured the pressure dependence of the PL of two $InAs/Ga_{1-x}In_xSb$ ($x=0.31$ and 0.25) superlattice samples. From these measurements, the pressure dependences of the valence-band offset for the two samples are estimated to be 3.5 ± 1.6 and 5.6 ± 2.5 meV/kbar.

ACKNOWLEDGMENTS

We thank W. B. Daniels for providing us with a SBC, and P. M. Young, H. Ehrenreich, and C. G. Van de Walle for helpful discussions. The work at Harvard was supported in part by the National Science Foundation under Grant No. DMR-91-23829.

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