Proposal for III-V ordered alloys with infrared band gaps

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It is shown theoretically that the recently observed spontaneous ordering of III-V alloys that yields alternate monolayer (111) superlattices provides the opportunity for achieving infrared band gaps in systems such as $(InAs)_1(InSb)_1$ and $(GaSb)_1(InSb)_1$. A substantial reduction in the *direct* band gap is predicted to result from the L-point folding that repel the Γ band-edge states.

Substantial effort has recently been focused on developing semiconductor materials for infrared (IR) devices in the wavelength range [illegible] above 8 μm. In addition to the use of intersubband absorption in tunnelling III-V superlattices,[2] four general physical principles have been previously utilized to directly shift band gaps into the IR spectral

(i) *Bulk alloying.* In this simple approach one uses the fact that alloy band gaps vary smoothly and continuously with composition (often with a parabolic deviation from linearity), and seeks a combination of mutually soluble [illegible] CdTe) semiconductors that produces a $(SG)_{1-x}(LG)_x$ alloy with a desired IR gap.

(ii) *Superlattice quantum confinement without strain.* The basic idea here is to take a semiconductor with a very [illegible] larger gap (LG). For small layer thicknesses (p,q), quan- [illegible] thus increasing the superlattice gap above that of pure SG.

(iii) *Superlattice strain induced* [illegible] gap and small lattice constant (SGSL) and layer it coherently with a material having a larger gap and larger lattice constant (LGLL), forming a strained-layer $(SGSL)_p/(LGLL)_q$ superlattice. Coherence of SGSL with LGLL interface, thus lowering its Γ conduction-band minimum. At the same time, tetragonal compression of SGSL in the perpendicular direction splits its VBM, raising the energy of the upper split components. Both effects act to reduce the band gap relative to unstrained bulk SGSL. This [illegible] $x > 0.61$. Since quantum confinement effects at small (p,q) act in the opposite direction, increasing the band gap, relatively thick layers can be used to achieve the [illegible] herently the misfit strain limits the maximum thickness that can be used.

(iv) *Superlattice-induced band inversion.* The basic of the constituents (AC) is lower in energy than the VBM of the other (BC); in this type of band lineup, the superlattice [illegible] stituents. This approach has been proposed by Arch *et al.*[8] for AC = InAs and BC = GaSb. Like in (iii) above, here, too, relatively thick layer would be required to counteract [illegible] II" band arrangement, thick layers deteriorate severely the intensity of optical absorption due to increased separation between electrons and holes. To reduce the layer thickness needed, the principle of "strain-induced band-gap reduc- [illegible] Mailhiot[9] for AC = InAs and BC = $Ga_{1-x}In_xSb$. This system was grown successfully by Chow *et al.*[10] where far-infrared photoluminescence was observed.

We discuss here a different principle of achieving infrared band gaps with III-V materials, namely "ordering [illegible] monolayer (001) oriented superlattices considered [illegible] point) folds into the Brillouin zone center. This leads to a

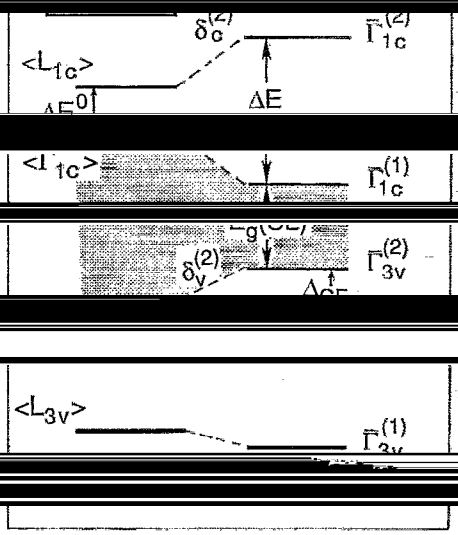

FIG. 1. Schematic plot of energy level shift at $\bar{\Gamma}$ of a typical III-V alloy [illegible]

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TABLE I. Calculated energy differences (eV) between the repelling states $\langle L_{1c}\rangle$ and $\langle \Gamma_{1c}\rangle$ before (ΔE^0) and after (ΔE) the perturbation potential is turned on. Values in parenthesis are for unrelaxed structures.

	GaAs/InAs	GaAs/InSb	GaAs/GaSb	InAs/InSb
$\Delta E^0 = \langle L_{1c}\rangle - \langle \Gamma_{1c}\rangle$	0.99	0.68	0.47	1.0
$\Delta E = \bar{\Gamma}_{1c}^{(2)} - \bar{\Gamma}_{1c}^{(1)}$	1.43 (1.22)	1.22 (1.02)	1.77 (1.28)	1.84 (1.39)
$R = \Delta E - \Delta E^0$	0.44 (0.23)	0.54 (0.34)	1.30 (0.81)	0.84 (0.39)

reduces the direct band gap, thus overwelming the opposite

ence between the superlattice states $\bar{\Gamma}_{1c}^{(2)}$ and $\bar{\Gamma}_{1c}^{(1)}$. Table I

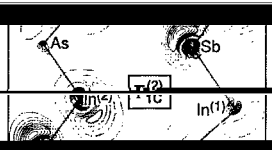
It has recently been noted[12] that numerous III-V alloys exhibit in vapor phase growth *spontaneous* long-range ordering in the form of monolayer $(AC)_1/(BC)_1$ superlattices in the (111) orientation (the "CuPt-like structure").

approximation (LDA), as implemented by the semirelativistic linearized augmented plane-wave (LAPW) method.[15] In all cases we have assumed that the superlattice is matched to a substrate whose lattice constant is the

CuPt ordering are given in Ref. 12. In all cases, ordering occurred as a result of *homogeneous* alloy growth *without*

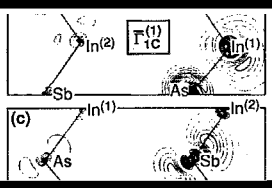
bution to R. This can be exemplified by the results for

point are constructed from the zincblende-like states at $\langle\Gamma\rangle + \langle L^{111}\rangle$. The folded zincblende states at this wave vector are coupled in the superlattice by the perturbing potential $\delta V(\mathbf{r}) = \delta V^{(\mathrm{chem})} + \delta V^{(\mathrm{size})}$ that has the symme-



As	0.003	0.014
$In^{(1)}$	0.023	0.071
Sb	0.350	0.086
$In^{(2)}$	0.453	0.012

size mismatch. This potential couples the alloy states and leads to a "level repulsion" between them, whereby superlattice states are displaced relative to the unperturbed (virtual crystal) states. For example, the $\bar{\Gamma}$-folding alloy states $\langle\Gamma_{1c}\rangle$ and $\langle L_{1c}\rangle$ couple through δV, producing the superlattice states $\bar{\Gamma}^{(1)}$ and $\bar{\Gamma}^{(2)}$ that are lowered and raised



Sb	0.120	0.001
$In^{(2)}$	0.088	0.014
As	0.000	0.190
$In^{(1)}$	0.000	0.010

The lowering of the CBM will be denoted (Fig. 1) as

produce the superlattice states Γ_{3v} and Γ_{3v} that are also mutually repelled (Fig. 1). The increase in the energy of the VBM will be denoted (Fig. 1) as $\delta^{(2)} = -\epsilon(\Gamma_{15v})$

Sb	0.029	0.005
$In^{(2)}$	0.020	0.076

mum at X is considerably higher in these systems[14] than $\bar{\Gamma}_1^{(1)}$, the former will not be discussed here.

To quantify the extent of level repulsion, we denote by ΔE^0 the $\langle L_{1c}\rangle - \langle \Gamma_{1c}\rangle$ energy difference *before* coupling

$(InAs)_1(InSb)_1$ in CuPt-like structure, plotted in the (110) plane. The contour step size is 4×10^{-3} e/au.^{3} Charges are normalized to 2 e/cell. On the right-hand side we also give the angular-momentum-and-site-decomposed charge (in units of e) for these states, where $In^{(1)}$ and $In^{(2)}$

TABLE II. Experimental low-temperature (LT) band gaps for the binary constituents and our predicted semirelativistic LDA-corrected low-temperature direct band gaps [Eq. (4)] for the four systems forming CuPt-like structure. The numbers in parenthesis are cystal field (denoted Δ_{CF} in Fig. 1) averaged values. The last row gives the change in the spin-orbit splitting $\delta\Delta_0$ relative to their respective averaged binary values. To include spin-orbit interactions, subtract 1/3 $\delta\Delta_0$ from E_g(SL). All energies are in eV.

	GaAs/InAs	GaSb/InSb	GaAs/InSb	InAs/InSb
E_g(binary)[a]	1.52/0.42	0.81/0.24	1.52/0.81	0.42/0.24
E_g(SL)[b]	0.55 (0.58)	0.09 (0.12)	0.27 (0.36)	−0.28 (−0.20)
$\delta\Delta_0$	−0.01	−0.01	0.08	0.08

[redacted] low-temperature values at Γ.

InAs/InSb: we find that without structural relaxation [where $\delta V(\mathbf{r}) = \delta V^{(\mathrm{chem})}(\mathbf{r})$] band coupling gives $R = 0.39$ eV, while after relaxation $\delta V^{(\mathrm{size})}(\mathbf{r})$ further increases R by an additional 0.45 eV.

the various states, as illustrated in Fig. 2 for $(InAs)_1/(InSb)_1$. We see that each member of a pair of coupling states ($\Gamma_{1c}^{1,2} + \Gamma_{3v}^{1,2}$ or $\Gamma_{1c}^{1,2} + \Gamma_{1v}^{1,2}$) has its charge localized [redacted] wave functions are localized on the In–As bonds, [redacted]

valence-band maximum $\overline{\Gamma}_{3v}^{(2)}$ is found to be localized systematically on the heavy atom semiconductor, while the conduction-band minimum $\overline{\Gamma}_{1c}^{(1)}$ is [redacted] strength of the VBM → CBM optical transition is predicted [redacted] SL repeat period is very short. We find that relaxation enhances substantially both the wave function localization and the mixing of s character into the valence-band-edge states [Fig. 2(d)] that are pure p states in the cubic binary constituents. This affects the spin-orbit splitting Δ_0.[11] Our predicted changes in the spin-orbit splitting $\delta\Delta_0 = \Delta_0[(AC)_1(BC)_1] - 1/2\ \Delta_0(AC) - 1/2\Delta_0(BC)$ are given in Table II. It shows that in the common-anion systems $\delta\Delta_0 \lesssim 0$, while for common-cation systems the negative bowing ($\delta\Delta_0 > 0$) is sizable.

dicted SL gap" E_g (SL) by subtracting the calculated level shifts (Fig. 1) from the experimental[16] (exptl) average of the gaps of the *constituents*

[redacted] E_g^{expt} [redacted]

This [redacted] LDA [redacted][11]

[redacted] larger lattice constant than the other partner. Consider-

(iii) above would therefore suggest that these SL's will have a larger band gap than the bulk constituent with the small gap. Table II shows, however, that in all cases except [redacted] strong level repulsion that overwhelms other effects. The

ergy denominators[11] ΔE^0 (Table I), consistent with a perturbation theory description. Indeed, since the L_{1c} level is closer in most alloys to Γ_{1c} than is X_{1c}, the level repulsion R in (111) SL's is larger than in (001) SL's [redacted]

Our semirelativistic calculations predict that in the [redacted] and $(InAs)_1/(InSb)_1$ will have direct band gaps of 0.09 [redacted] the systems are not perfectly ordered. For example, for [redacted] given composition x one has additional control over the band gap through variations of the growth parameters that [redacted][13] Experimental [redacted]

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[redacted]

binary constituents (Table II) and $b \approx 0.6$ eV (Ref. 16) is the bowing