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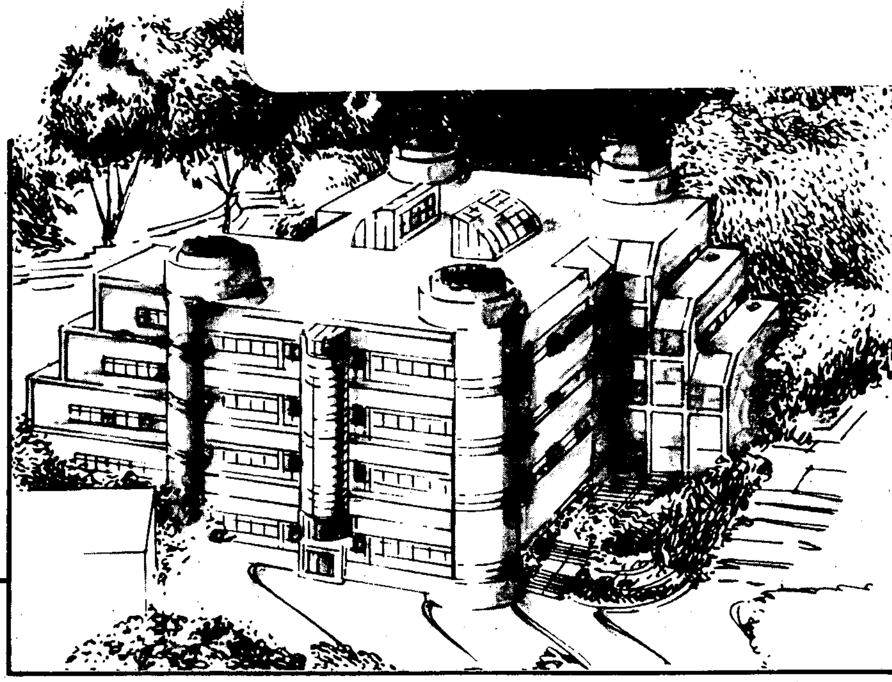

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Abstract:

Recently determined band-edge hydrostatic deformation potentials are used to predict heterojunction band offsets for the pseudomorphic GaAs-InP system. The calculations include GaAs/InP, InP/GaAs, and strained-layer GaAs-InP superlattices for both [100] and [111]-oriented epitaxial growth. The offsets are Type-II for the unstrained case. The large hydrostatic contributions to the stress-induced band offsets can convert the offsets to Type-I. This conversion is especially apparent for growth in the [111]-direction because of the small Poisson's ratio for biaxial stress in the (111)-plane.

Many hetero-epitaxial devices rely on the matching of lattice constants between the substrate and the epitaxial layer. There are many examples of these lattice-matched systems, most notably the AlGaAs-GaAs system, and $InP/In_{0.53}Ga_{0.47}As$ which is an important heterostructure used for optoelectronic applications in the wavelength range from 1.3 to 1.5 μm. However, the requirement of lattice-matching restricts the use of the otherwise wide variety of properties among the semiconductor alloys. Currently, attention is being focused on the growth and use of epitaxial layers that are coherently strained to match the lattice constant of the substrate[1,2], and also of strained-layer superlattices in which the strain is taken up by both materials[3]. These layers can sustain large biaxial strains of several percent, depending on the thickness of the layer[4,5]. The large strains lower the crystal symmetry and can strongly alter the electronic properties of the strained "pseudomorphic" layer. The band-edge discontinuities at the interface between the strained pseudomorphic layer and hte substrate can have large stress-induced contributions. The biaxial coherency strain has shear components, as well as hydrostatic components. The hydrostatic component is defined as the volume change caused by the biaxial stress. The volume change depends on the unstrained lattice mismatch, as well as on the Poisson's ratio for the specific growth direction. The hydrostatic contribution to the band offset at a strained-layer interface is given by

$$\Delta E^{hyd} = a\,\Delta \quad , \qquad (1)$$

where a is the band-edge hydrostatic deformation potential with units of energy per unit strain, and Δ is the volume strain of the strained layer. Until recently, hydrostatic band-edge deformation potentials were not available, causing uncertainty in the predictions of strained-layer band offsets[6,7]. Recent theoretical efforts to predict the band offsets at strained-layer interfaces have had reasonable success for a limited number of materials and growth orientations[8,9]. Most calculations and experiments have concentrated on growth in the [100]-direction, while little attention has been payed to the properties of strained epitaxial growth in the [111]-direction. Interest in [111]-growth is increasing because of the possibility of incorporating large polarization fields caused by the large strains and the piezoelectric effect in the

III-V semiconductors[10]. In this paper, recently determined band-edge hydrostatic deformation potentials[8,11,12,13] are used to predict the band offsets of GaAs/InP, InP/GaAs and strained-layer GaAs-InP superlattices for [111] and [100] oriented growth. The hydrostatic contributions to the band offsets are large for this system. In fact, the difference in Poisson's ratio for <111> compared to <100> directions can lead to Type-I or Type-II superlattices, depending on the growth orientation and substrate material.

The volume strain is derived as the trace of the strain tensor. When a semiconductor with lattice constant d_e is grown epitaxially on a [100] oriented semiconductor substrate with lattice constant d_s, the strain is assumed to be constrained entirely in the epitaxial layer. For this case the strain tensor is

$$\varepsilon_{ij}=\frac{\left(\frac{d_s}{d_e}-1\right)}{\left(s_{11}+s_{12}\right)}\begin{pmatrix}\left(s_{11}+s_{12}\right) & 0 & 0\\ 0 & \left(s_{11}+s_{12}\right) & 0\\ 0 & 0 & 2s_{12}\end{pmatrix}. \qquad (2)$$

The corresponding volume strain is

$$\Delta=\frac{2\left(s_{11}+2s_{12}\right)}{\left(s_{11}+s_{12}\right)}\left(\frac{d_s}{d_e}-1\right) . \qquad (3)$$

The strain tensor for [111]-oriented epitaxial growth is

$$\varepsilon_{ij}=\frac{\left(\frac{d_s}{d_e}-1\right)}{\left(s_{11}+2\,s_{12}+\frac{1}{4}\,s_{44}\right)}\begin{pmatrix}\left(s_{11}+2\,s_{12}\right) & -\frac{1}{4}s_{44} & -\frac{1}{4}s_{44}\\ -\frac{1}{4}s_{44} & \left(s_{11}+2\,s_{12}\right) & -\frac{1}{4}s_{44}\\ -\frac{1}{4}s_{44} & -\frac{1}{4}s_{44} & \left(s_{11}+2\,s_{12}\right)\end{pmatrix} \qquad (4),$$

with the corresponding volume strain

$$\Delta = \frac{3\left(s_{11}+2s_{12}\right)}{\left(s_{11}+2s_{12}+\frac{1}{4}s_{44}\right)}\left(\frac{d_s}{d_e}-1\right) \qquad (5).$$

For the equilibrium strained-layer superlattice, both materials deform. The strain condition is derived assuming continuous stress across the heterojunction interface. The above equations (2 - 5) are modified by replacing d_s with the new equilibrium lattice constant d_{eq} common to both materials:

$$d_{eq} = \frac{1+r}{\frac{1}{d_{GaAs}}+\frac{r}{d_{InP}}} \qquad (6)$$

where

$$r = \frac{\left(s_{11}+s_{12}\right)_{GaAs}}{\left(s_{11}+s_{12}\right)_{InP}} \quad \text{for} \quad [100]$$

$$r = \frac{\left(s_{11}+2\,s_{12}+\frac{1}{4}s_{44}\right)_{GaAs}}{\left(s_{11}+2\,s_{12}+\frac{1}{4}s_{44}\right)_{InP}} \quad \text{for} \quad [111].$$

The hydrostatic contributions to the band offsets for GaAs/InP, InP/GaAs and GaAs-InP strained superlattice are given in Table I based on eq.(1) and on the material properties given in Table II. The error in the hydrostatic band offset is ±50 meV. The volume strains are clearly larger for growth in the [111] direction, yielding larger hydrostatic contributions to the band offsets. This is because of the smaller Poisson's ratio for <111>-directions compared to <100>-

directions. The material does not contract or expand as much in the [111]-direction in response to the in-plane strain as it does for [100]-growth.

For the direct gap semiconductors GaAs and InP, the conduction bands are unaffected to lowest order by shear strain, but the degenerate Γ_8 valence bands are split by the shear strain into two doublets: X_6 and X_7 of D_{2d} symmetry for [100]-oriented growth, and into Λ_4 and $\Lambda_{5,6}$ of C_{3v} symmetry for [111]-oriented growth. The influence of strain on hole mobility has motivated previous research into the splitting of the valence band in strained-layers[14,15,16]. The energy shift of the top valence band edge is given in the limit of infinite splin-orbit splitting by[17]

$$\Delta E^2 = \frac{b^2}{2}\left[(\varepsilon_{xx}-\varepsilon_{yy})^2+(\varepsilon_{xx}-\varepsilon_{zz})^2+(\varepsilon_{yy}-\varepsilon_{zz})^2\right] + d^2\left[\varepsilon_{xy}^2+\varepsilon_{xz}^2+\varepsilon_{yz}^2\right] \quad (7)$$

Under the large strains in the strained-layer, the coupling of the X_7 (Λ_4) band (split from the original Γ_8 band) with the X_7 (Λ_4) split-off band cannot be ignored. The energy shifts of the top valence band in the presence of this coupling are

Biaxial compression: $E = \Delta E$

Biaxial tension: $$E = \frac{\Delta E}{2} - \frac{\Delta_{so}}{2} + \frac{\Delta_{so}}{2}\sqrt{1 + 9\left(\frac{\Delta E}{\Delta_{so}}\right)^2 + 2\left(\frac{\Delta E}{\Delta_{so}}\right)} \quad (8)$$

The coupling to the split-off band has no effect for biaxial compression of the strained-layer because in this case the X_6 ($\Lambda_{5,6}$) band, which is the band that moves into the bandgap, does not couple to the split-off band. Under biaxial tension, however, the X_7 bands mix, increasing the upwards shift of the bandedge. The contributions of the shear strain to the valence band offsets are given in Table I based on the material properties of Table II.

The stress-induced band offsets must be added to the original, unstrained band offsets to obtain the band offsets for the pseudomorphic junction. Band offsets have been predicted successfully with the use of the transition-metal line-up principle[18]. Based on the energy positions of 3d transition metal levels in GaAs and InP, the following unstrained band discontinuities are ascribed:

$$\Delta E_c = E_c(\mathrm{GaAs}) - E_c(\mathrm{InP}) = 0.3 \text{ eV}$$
$$\Delta E_v = E_v(\mathrm{GaAs}) - E_v(\mathrm{InP}) = 0.2 \text{ eV}.$$

The positive signs for both values indicate a Type-II heterojunction for the unstrained situation. When the stress-induced shifts are added to these unstrained offsets, the pseudomorphic band offsets result. These are listed in Table I and are shown in Fig. 1. For the case of [100]-growth, the heterojunction remains Type-II, or marginally converts to Type-I, although no strong statements about the conversion can be made because of the uncertainty in the material properties. In sharp contrast, for [111]-growth the heterojunction clearly converts to Type-I for the case of pseudomorphic-GaAs on InP and for the strained superlattice.

In conclusion, the band offsets for the pseudomorphic InP/GaAs system have been predicted for [100] and [111]-oriented epitaxial growth. The large conduction band hydrostatic deformation potentials of these direct-gap materials lead to large shifts of the pseudomorphic conduction band-edges. A direction-dependent conversion of the band offsets from Type-II to Type-I is proposed, caused by different Poisson's ratios for different growth directions. The smaller Poisson's ratio for [111]-oriented growth produces larger volume strains and consequently larger hydrostatic shifts compared to [100], yielding strong type conversion for [111]-oriented strained layers. This lattice mis-match type-conversion may provide additional design flexibility to the already wide variety of material properties among the compound semiconductor heterostructures.

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Tables:

Table I. Band Offsets (eV) (± 0.05 eV)

		epi [substrate]		superlattice
		GaAs [InP]	**InP [GaAs]**	**GaAs - InP**
Stress Contributions to Band-Edge Offsets				
[100]	Δ	+4.2 %	-3.1 %	+2.1 % -1.8 %
	ΔE_c^{hyd}	-0.38	+0.22	-0.29
	ΔE_v^{hyd}	-0.02	+0.01	-0.01
	ΔE_v^{ax}	+0.23	+0.16	-0.01
[111]	Δ	+5.9 %	-4.9 %	+2.7 % -2.6 %
	ΔE_c^{hyd}	-0.54	+0.34	-0.43
	ΔE_v^{hyd}	-0.02	+0.02	-0.02
	ΔE_v^{ax}	+0.28	+0.18	0.00
Band-Edge Offsets				
[100]	ΔE_c	-0.08	+0.08	+0.01
	ΔE_v	+0.41	+0.07	+0.18
[111]	ΔE_c	-0.24	-0.04	-0.13
	ΔE_v	+0.45	0.00	+0.18

Table II: Semiconductor properties*

	GaAs	InP
a_0	5.65 Å	5.87 Å
s_{11}	0.0118 GPa^{-1}	0.016 GPa^{-1}
s_{12}	-0.0037 GPa^{-1}	-0.0059 GPa^{-1}
s_{44}	0.0169 GPa^{-1}	0.022 GPa^{-1}
b	-2.0 eV	-2.0 eV
d	-5.3 eV	-5.0 eV
†a_c	-9 eV	-7 eV
†a_v	-0.4 eV	-0.4 eV
Δ_{so}	340 meV	110 meV
$\nu[100]$	-0.31	-0.37
$\nu[111]$	-0.19	-0.26

$E_c(GaAs) - E_c(InP) = 0.3$ eV

$E_v(GaAs) - E_v(InP) = 0.2$ eV

*From Landölt-Burnstein, vol. 17a 1984

†From Nolte et al., Phys. Rev. Lett. **59**,501(1987)

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Figures:

Fig. 1 Band offsets for the pseudomorphic GaAs-InP system. The material in brackets is the substrate. The offsets in the unstrained case are Type-II. The large hydrostatic contributions to the strained-layer offsets can drive the offsets to Type-I for some situations, most notably for growth in the [111]-direction because of the smaller Poisson's ratio for this direction.

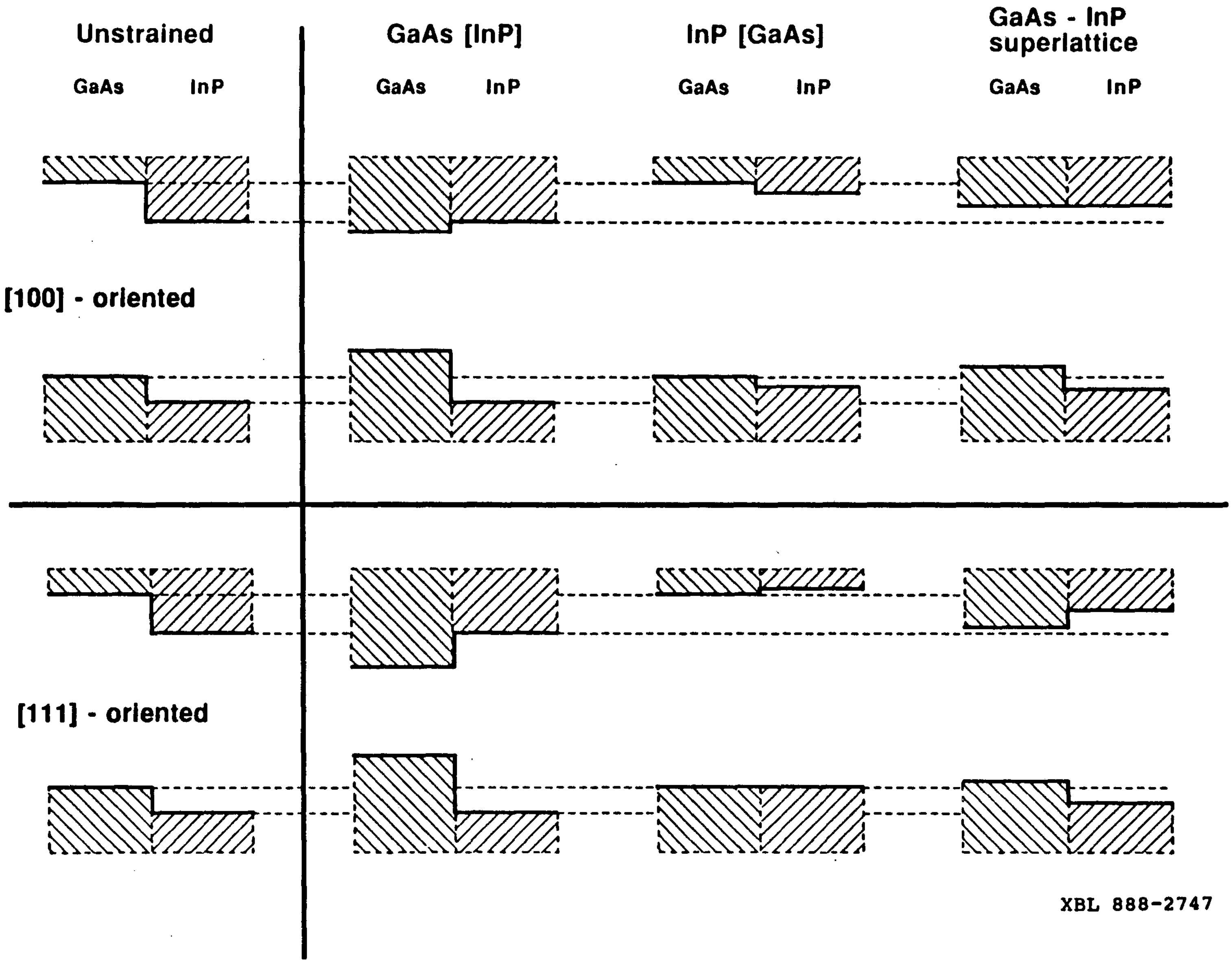
Unstrained
GaAs [InP]
InP [GaAs]
GaAs - InP
superlattice
GaAs
InP
GaAs
InP
GaAs
InP
GaAs
InP
[100] - oriented
[111] - oriented
XBL 888-2747

Figure 1.