NOTE: The original publication of this article contained the incorrect artwork. The following presents the paper as it should have originally appeared.

Interface Strain in Organometallic Vapor Phase Epitaxy Grown InGaAs/InP Superlattices

A.R. CLAWSON, X. JIANG, and P.K.L. YU

University of California, San Diego, Department of Electrical and Computer Engineering, La Jolla, CA 92093-0407

C.M. HANSON and T.T. VU

Naval Command Control Ocean Surveillance Center RDTE DIV, San Diego, CA 92152-5000

The spatial distribution of strain in organometallic vapor phase epitaxy grown InGaAs/InP superlattice structures has been studied by varying the thicknesses of the InGaAs well and the InP barrier layers and measuring the strain. High resolution x-ray diffraction rocking curves were used to measure the strain from angular separation between the zeroth-order superlattice peak and the substrate (004) peak. The results are consistent with a compressive strain resulting from arsenic carryover into the InP following InGaAs growth. The strain is not localized at the interfaces but extends into the InP barrier layer. The amount of arsenic carryover increases with the growth time of the InGaAs well.

Key words: InP/InGaAs superlattice, interfacial strain, organometallic vapor phase epitaxy (OMVPE)

INTRODUCTION

Vapor phase growth techniques using organometallics are convenient for fabricating heterojunction epilayers and superlattices of InGaAs/InP because they can provide easy control of growth rates and layer compositions for complicated multilayer structures. Many new quantum engineered devices using these materials are being proposed for high speed electronic and photonic applications. However, there continues to be questions as to how best to produce abrupt heterojunctions needed for devices. Although heterojunction interfaces of single quantum wells are reported to be abrupt and flat judging from photoluminescence spectra, in superlattice structures there is evidence of interface induced strain and of compositional intermixing, the latter seeming to occur particularly at the InP grown on InGaAs interface.

Compressive strain is evident from x-ray diffraction (XRD) rocking curves of all superlattice structures grown with our reactors, and similar strain has been reported or is evident from XRD results of other investigators. The magnitudes of this strain are remarkably similar for both organometallic vapor phase

epitaxy (OMVPE)¹⁻³ and gas source molecular beam epitaxy (GSMBE)⁴⁻⁶ growth. Explanations for the strain come primarily from two points of view, either the existence of an intrinsic heterojunction interface strain resulting from atomic bond length differences between one composition semiconductor to another,^{5,7} or compositional intermixing across the interface causing alloyed regions of different lattice constant.^{2,4} A third possibility is that the composition of very thin InGaAs quantum wells is different from that of thick epilayers. However, from an experimental check, we find identical compositions from InGaAs grown both as composites of discrete very thin layers separated by growth interrupts and as continuously grown thick layers.³ Also, Meyer et al.² have shown that InGaAs layer compositions have the same In/Ga proportion as the source gas and behave as though the same composition is maintained in quantum well films. We are confident that compositional variation on the Group III sublattice is negligible compared to variation on the Group V sublattice.

Arguments for an intrinsic interface strain are very convincing. Since the demonstration by Mikkelsen and Boyce⁸ that the nearest neighbor InAs and GaAs bond lengths in InGaAs are only slightly changed from their binary compound spacing, it is apparent

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that the spacing across an InP/InGaAs heterojunction will maintain the nearest neighbor bond lengths of the paired atoms and depend on the specific sequence of atoms across the interface. Hybertsen⁷ shows that one possible result can be a significant compressive strain as we observe, which is localized across the heterojunction interface. Vandenberg et al.⁵ verified by GSMBE growth that the strain can be affected by the sequencing of the deposited layers.

On the other hand, there is also considerable evidence that compositional intermixing is the primary cause of strain. Although the InGaAs grown on InP interface abruptness is confirmed by two-dimensional electron gas studies⁹ and by photoluminescence analysis,¹⁰ the InP grown on InGaAs is less ideal. High resolution transmission electron microscopy shows a composition transition region.^{11,12} Spycher et al.¹² attribute the interface region to carryover of arsenic into InP, resulting in a region of InAsP that would give a compressive strain consistent with our XRD results. Arsenic-carryover is also proposed as the cause of photoluminescence spectra shifts to lower than expected energies in very thin quantum wells.¹⁰ In our reactor, arsenic-carryover is evident from secondary ion mass spectrometry analysis of InP grown on 1 μm thick InGaAs layers³ and is expected to also be a problem in the thin layer growth. The arsenic-carryover appears to be a memory effect resulting from residual arsenic in the growth chamber following growth of InGaAs.

Other mechanisms for compositional intermixing besides carryover of a residual constituent are from exposure of InP to arsine and of InGaAs to phosphine at elevated temperatures, both of which result in exchange of the Group V constituent to form an alloyed surface.^{10,13} In this study, we have tried to use growth conditions to minimize interface alloying contributions by reducing cross-exposure to the Group V hydrides.

Optimizing lattice-match in superlattices has been dealt with in several ways. Our approach has been to deliberately adjust the InGaAs composition to be slightly gallium-rich in order to adjust the superlattice to lattice match the InP substrate as determined by x-ray diffraction. The excess gallium introduces a tensile strain in the InGaAs wells, which we deduce is needed to balance a compressive strain associated with the heterojunction interfaces. We have tried several growth interrupt schemes to reduce strain and optimize the interface abruptness, with little improvement. Unfortunately, any reduction of the observed compressive strain appears to be by compensation with inverse strain rather than by its elimination.¹⁴

Proposed descriptions of the location and magnitude of the interface strain have been made by several investigators using simulations of x-ray diffraction patterns to best fit the measured superlattice satellite peak positions and intensities.^{4,5,14,15} Good agreement has been achieved by assuming various forms of strained interface regions, although there is

considerable variety to their proposed nature. Some of the better fits occur when an interface region of a fairly thick InAsP ternary, with low arsenic concentration, is introduced at the InP grown on InGaAs transition.^{4,14} Good fits are also reported for combinations of thin, highly strained interface regions at both interfaces.^{2,5,15} Rather than relying on inference from x-ray pattern simulations, we have addressed the issue of how the strain is distributed in InGaAs/InP superlattices by analyzing the change of measured strain as InGaAs well and InP barrier layer thicknesses are varied. Our results show that the strain is dependent on both the well and barrier thicknesses in a manner that can best be interpreted as due to arsenic carryover extending a considerable distance into the InP barrier layers following InGaAs growth.

DESCRIPTIVE MODEL

Strain of the superlattice is described by elastic tetragonal distortion of a cubic lattice that is constrained to the InP substrate lattice spacing in the interface plane. The distortion stresses (the forces distorting the lattice) are relieved by the elastic expansion or contraction of the layer lattice in the unconstrained dimension perpendicular to the substrate. The strain (the equilibrium distortion of the lattice) is measured by high resolution x-ray diffraction of the lattice spacing perpendicular to the substrate. For the superlattice, lattice-match is determined by the superposition of its zeroth-order peak with the substrate (004) peak, requiring the superlattice spacing to be an integral number of InP lattice spacings. However, within a superlattice period, localized strained layer regions can exist, and lattice-match only requires that the localized strains balance out to give an average InP lattice spacing. The strain values reported here are derived from the measured tetragonal distortion as $\Delta a/a = 1/2 \Delta d/d$, which is close to the exact Poisson ratio corrections for the Group III-V compositions of InP and $\text{In}_{.53}\text{Ga}_{.47}\text{As}$.¹⁶ We ignore small differences in the elastic constants of the materials that locally strain the superlattice, and assume the superlattice to be an elastic medium with compositionally independent elastic constants in which stresses can be adjusted by local composition variations.

To analyze the effects of changing well and barrier thicknesses on the measured superlattice strain, we propose the simple model of Fig. 1 in which the stresses distorting the lattice are distributed in four distinct regions: the InP barrier, the InGaAs well, a strained interfacial region from barrier to well (I_1), and a strained interfacial region from well to barrier (I_2). General features of this model are

- the strain in a single period of thickness d_{SL} represents the entire repeated superlattice,
- the thickness d_{b} is pure InP that is unstrained since the lattice parameter in the interface plane is constrained to that of the thick InP substrate,
- the thickness d_{w} is of uniform composition InGaAs, strained by its mismatch from InP, and

• interface regions I_1 and I_2 are of unknown thicknesses and must be part of either or both the intended well and barrier thicknesses m and n . The interface strains can be of mixed tensile and compressive components.

It is difficult to discriminate the individual interface strain contributions of regions I_1 and I_2 ; however, we know that the compressive strain observed in the superlattices can only occur if the arsenic were to alloy with the InP barrier, or if excess indium were to alloy with the InGaAs well. Since our direct evidence is that arsenic is alloying into the InP, we propose that compositional mixing by arsenic carryover from InGaAs to InP is the dominant strain mechanism, and we will interpret our experimental results based on this premise. We will show that the data are fully consistent with this interpretation.

To reduce the number of variables in the model of Fig. 1, we make some simplifying assumptions:

- Interface I_1 has negligible strain, thus thickness $d_1 = 0$ and all the interface strain is associated with arsenic carryover at I_2 .
- No interface strain exists in the InGaAs well, thus thickness $d_w = m$, as intended.
- With the arsenic-carryover, all the I_2 interface strain exists within the intended InP barrier thickness n , thus $n = d_b + d_2$.

The overall strain within the superlattice period is the sum of the individual layer spacings that we have grouped into the regions of Fig. 1. This provides an easy way to quantitatively assess the results. We propose that the relationship of the strains relevant to the measurable data is

$$S_{(\text{measured})} = S_{(\text{InGaAs})} + S_{(\text{interface})} \quad (1)$$

where the integrated strain over a superlattice period is $S_{(\text{measured})} = \Delta a/a_{(\text{measured})} \times \text{period thickness, } d_{\text{SL}}$, the integrated InGaAs mismatch strain (usually tensile) is $S_{(\text{InGaAs})} = \Delta a/a_{(\text{InGaAs})} \times \text{well thickness, } m$, and the integrated compressive interface region strain is $S_{(\text{interface})} = \Delta a/a_{(\text{interface})} \times \text{thickness of the interface region, } d_2$. We can determine $\Delta a/a_{(\text{measured})}$ and d_{SL} from XRD data, and we can determine $\Delta a/a_{(\text{InGaAs})}$ from the growth composition and m from the growth rate. Therefore, we can solve for $S_{(\text{interface})}$.

EXPERIMENTAL

A series of growths under identical conditions was performed of structures based on the 70Å InGaAs/140Å InP, 30 period lattice-matched superlattice as a reference structure. The intended well and barrier thicknesses (based on their growth rates and times) were independently varied and the number of periods adjusted to keep the superlattice thicknesses at ~6300Å. The growth was from trimethylindium, trimethylgallium, arsine, and phosphine at 650°C, 20 Torr, in a lamp heated horizontal reactor. The group V/III gas ratios were 160 for the InP barriers and 95 for the InGaAs wells. We have discussed elsewhere other details of the reactor and growth procedures.³ Particular care was taken to use a conditioned growth

Fig. 1. A model for discussing the effect of strained regions in the vicinity of the interfaces in InGaAs/InP superlattices. The behavior of the two interfaces is expected to be different because of the difference in growth chemistries as the compositions are reversed. Strains associated with the interfaces are assumed located in the regions I_1 and I_2 , and there is no designation as to whether the strained regions are in the InP, the InGaAs, or both. The InGaAs well exclusive of the interfaces is of uniform composition. The InP barrier exclusive of the interfaces is the true binary with no alloyed components.

Fig. 2. Experimental strain $\Delta a/a_{(\text{measured})}$ dependence for varying the intended barrier thickness n in an m Å InGaAs well/ n Å InP barrier-6500 Å thick superlattice grown by OMVPE with the well thicknesses fixed at $m = 40$ Å and 70 Å. The InGaAs composition was fixed to provide lattice-match for a 70 Å well/140 Å barrier superlattice. The $n = 0$ data point was specified for the limiting case of all $\text{In}_{.485}\text{Ga}_{.515}\text{As}$, the fixed ternary composition.

chamber to achieve the reproducibility necessary to compare small changes in strain since both the composition and growth rate are affected by the nature of sidewall deposits in the chamber. Growth interrupts of two seconds under hydrogen at each interface were used to minimize intermixing of arsine and phosphine without introducing other interface alloying. The InGaAs solid composition quoted below was determined from the proportional change of In/Ga gas composition referenced to that used to achieve a nominal $\text{In}_{.53}\text{Ga}_{.47}\text{As}$ lattice-matched thick epilayer.

Fig. 3. Spatial distribution of compressive strain $\Delta a/a_{(\text{interface})}$ in the InP barrier layer following growth of InGaAs well layers of thickness $m = 40\text{Å}$ and 70Å . The results are extracted from the interpolated curve fit of Fig. 2 by calculating the incremental decrease in $\Delta a/a_{(\text{measured})}$ from the slope of the curve and attributing it to $\Delta a/a_{(\text{interface})}$ in the InP. Also given is the corresponding composition of $\text{InAs}_x\text{P}_{1-x}$ assuming the strain is the result of arsenic carryover.

Fig. 4. Experimental strain $\Delta a/a_{(\text{measured})}$ dependence for varying the intended well thickness m in an $m\text{Å}$ InGaAs well/140Å InP barrier-6300Å thick superlattice grown by OMVPE. The InGaAs composition was that needed to provide lattice-match for $m = 70\text{Å}$. The $m = 0$ data point was specified for the limiting case of all InP with no InGaAs. The XRD measured strain $\Delta a/a_{(\text{measured})}$ is corrected to values for a relaxed lattice.¹⁶

X-ray diffraction rocking curves were performed on (004) reflections with $\text{CuK}\alpha_1$ radiation from a four crystal monochromator.

RESULTS AND DISCUSSION

Results of varying the InP barrier thickness while holding the InGaAs composition and well thickness constant are shown in Fig. 2 for two well thicknesses, 40Å and 70Å. The expectation for the 70Å well superlattice that is lattice matched for large barrier

thickness is that overall strain will be unchanged as the unstrained InP portion d_b of the barrier thickness n in Fig. 1 is decreased to $d_b = 0$. As the thickness d_2 of the compressively strained alloyed interface region I_2 decreases, the strain $\Delta a/a_{(\text{measured})}$ becomes increasingly tensile due to the fixed gallium-rich InGaAs tensile contribution. Unfortunately, data for InP barrier thicknesses of less than $n = 40\text{Å}$ were not obtainable due to difficulty in achieving superlattice growth when the barriers are very thin. The limiting strain of $\Delta a/a_{(\text{measured})} = -0.32\%$ at barrier thickness $n = 0$ is for the fixed $\text{In}_{.485}\text{Ga}_{.515}\text{As}$ composition that was necessary to achieve lattice-match in the 70Å/140Å superlattice. The data show that a compressively strained interface region extends $\sim 100\text{Å}$ into the InP. The solid curves of Fig. 2 are interpolations of the few available data points; nevertheless, they behave as a reasonable fit from which we can extract the $\Delta a/a_{(\text{interface})}$ spatial distribution.

We are given that 70 and 40Å wells of uniform $\text{In}_{.485}\text{Ga}_{.515}\text{As}$ have a tensile integrated strain of $S_{(\text{InGaAs})} = 70\text{Å} \times -0.32\% = -0.224$ and $S_{(\text{InGaAs})} = 40\text{Å} \times -0.32\% = -0.128$, respectively. In Fig. 2, the measured strain $\Delta a/a_{(\text{measured})}$ shows that for small barrier thicknesses of $n < d_2$ the entire layer is compressively strained, presumably from arsenic carryover. Only when the barrier layer thickness n is greater than d_2 is the InP layer thick enough to totally compensate the tensile strain, so that thicker layers only add unstrained, or pure, InP. From the difference between the InGaAs well strain $S_{(\text{InGaAs})}$ and incremental change of $\Delta a/a_{(\text{measured})}$ with increasing barrier thickness n (i.e. from the slopes of the curves in Fig. 2), we can derive the distribution of $\Delta a/a_{(\text{interface})}$ as shown in Fig. 3. The arsenic concentration x of the corresponding $\text{InAs}_x\text{P}_{1-x}$ alloy is also shown. The exact shapes of the arsenic distributions in Fig. 3 are somewhat tentative because of their extraction from the interpolated curves of Fig. 2. The region within $\sim 20\text{Å}$ of the InGaAs interface is particularly uncertain due to the steep slopes and the absence of data points. Mainly the flatness of the profile near the interface is questionable. Also, one might expect the arsenic concentrations near the interface to be the same for both the 40 and 70Å well thickness. The discrepancy could result either from inaccuracies in our data or from other strain contributions that we had considered to be negligible. Nevertheless, the integrated compressive strain $S_{(\text{interface})}$ fixes the area under the curves in Fig. 3, and the data confirm that the strain is deeply distributed into the InP.

The effect of changing the InGaAs well thickness m is shown in Fig. 4. In this case, the InP barrier thickness is fixed at $n = 140\text{Å}$, and $\Delta a/a_{(\text{measured})}$ is zero (i.e. lattice-matched) when $m = 70\text{Å}$. Qualitatively, we expect $\Delta a/a_{(\text{measured})}$ to increase (negative sign) due to the increased tensile strain of the gallium-rich InGaAs for $m > 70\text{Å}$ and to increase (positive sign) for $m < 70\text{Å}$ as the tensile strain is reduced. At $m = 0$, the strain must reduce to zero for the limiting case of only InP growth. The small magnitude of the strains in Fig. 4

indicates that both the tensile InGaAs strain in the well and the compressive InAsP strain in the barrier are dependent on the thickness (i.e. growth times) of the wells. The strain $\Delta a/a_{(\text{measured})}$ is determined from the sum of large numbers of opposite sign between a

Fig. 5. The dependence of arsenic carryover into InP barrier layers on the thickness m of the InGaAs well layer, determined by calculating $S_{(\text{interface})}$ from the data of Fig. 4. The arsenic concentration is expressed as equivalent monolayers of InAs; however, its distribution in the InP will be in the manner of Fig. 3.

Table I. Compressive Strain in InGaAs/InP Superlattices

Superlattice Structure [InGaAs/InP]	Interface Integrated Strain [thickness (Å) $\times \Delta a/a$]*	Equivalent Added InAs to Cause Strain	Ref.
70Å/140Å (OMVPE)	0.224 ^a	2.4 ML	this work
85Å/167Å (GSMBE)	0.238 ^a 0.188 ^b	2.5 ML 2.0 ML	5
73Å/73Å (CBE)	0.167 ^b	1.8 ML	4
100Å/200Å (OMVPE)	0.162 ^a	1.7 ML	1
30Å/330Å (OMVPE)	0.122 ^b 0.156 ^a	1.3 ML 1.7 ML	2
112Å/36Å 38Å/130Å (OMVPE)	0.320 ^a 0.264 ^a	3.4 ML 2.8 ML	14

* Determined using Eq. 1.

^a From $\Delta a/a_{(\text{InGaAs})}$ as determined from the InGaAs composition and $\Delta a/a_{(\text{measured})}$.

^b From interface strain, $S_{(\text{interface})}$ as the sum of the author's proposed interface monolayer contributions.

tensile integrated strain $S_{(\text{InGaAs})}$ and a compressive interfacial integrated strain $S_{(\text{interface})}$. Using Eq. 1, we can calculate from $a_{(\text{measured})}$ of Fig. 4, the dependence of arsenic-carryover integrated strain $S_{(\text{interface})}$ on the well thickness m as shown in Fig. 5. The arsenic carryover increases as the well growth time increases.

The exact cause of the observed arsenic carryover is not understood. The use of hydrogen-only interrupts to purge excess arsine following InGaAs growth shows only small change in the compressive strain,³ thus the arsenic-carryover must come from some source other than the controlled flows of arsine and phosphine for which switching times are expected to be less than 1 sec. We attribute the contaminating arsenic to residuals from desorption of adsorbed gases or vaporization of heated solid deposits on the sidewalls and the susceptor, although some other interaction fundamental to the growth of InP on InGaAs may occur.

A comparison of the compressive strain in InGaAs/InP superlattices derived using Eq. 1 for results reported in the literature is given in Table I. There are differences in the various reported layer thicknesses; but even when these are taken into account, the similarity in magnitude of compressive strains is remarkable considering the scope of growth techniques. Generally, the strain is greater for thicker InGaAs wells consistent with our results. An equivalent compressively strained interface layer expressed as monolayers (ML) of InAs is shown for comparison. The issue of arsenic carryover seems to be a problem common to most InGaAs/InP superlattice growth.

CONCLUSIONS

The strain of OMVPE grown InGaAs/InP superlattices relative to lattice-match with an InP (100) substrate varies in a manner consistent with compositional mixing resulting from arsenic carryover into the InP barrier following growth of the InGaAs well. A compressive strain proportional to arsenic concentration in the InP decreases away from the InGaAs interface over a range of $\sim 100\text{\AA}$. The measured strain is the sum of two dominant components—the InP arsenic-carryover component and the InGaAs compositional mismatch component. There is no evidence of a large localized compressive strain right at the interfaces, however, existence of localized balanced interface strains cannot be excluded. Change of strain with change of well thickness shows the amount of arsenic carryover to depend on the length of exposure of the chamber to arsine during InGaAs growth. The degree of the observed arsenic carryover may be related to our specific apparatus and growth conditions; however, the presence of similar compressive strain in other investigators' InGaAs/InP superlattices suggests that arsenic carryover may be a limiting mechanism in achieving ideal heterojunctions for InP grown on InGaAs.

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REFERENCES

1. H. Kamei and H. Hayashi, *J. Cryst. Growth* 107, 567 (1991).
2. R. Meyer, H. Hardtdegen, R. Carius, D. Grützmacher, M. Stollenwerk, P. Balk, A. Kux and B. Meyer, *J. Electron. Mater.* 21, 293 (1992).
3. A.R. Clawson, T.T. Vu, S.A. Pappert and C.M. Hanson, *J. Cryst. Growth* 124, 536 (1992).
4. A. Antolini, P.J. Bradley, C. Cacciato, D. Campio, L. Gastaldi, F. Genova, M. Iore, C. Lamberti, C. Papuzza and C. Rigo, *J. Electron. Mater.* 21, 233 (1992).
5. J.M. Vandenberg, M.B. Panish, R.A. Hamm and H. Temkin, *Appl. Phys. Lett.* 56, 910 (1990).
6. M.E. Sherwin, F.L. Terry, Jr., G.O. Munns, J.S. Herman, E.G. Woelk and G.I. Haddad, *J. Electron. Mater.* 21, 269 (1992).
7. M.S. Hybertsen, *J. Vac. Sci. Technol. B* 8, 773 (1990).
8. J.C. Mikkelsen and J.B. Boyce, *Phys. Rev. Lett.* 49, 1412 (1982).
9. P.J.A. Thijs, J.M. Lagemaat and R. Woltjer, *Electron. Lett.* 24, 226 (1988).
10. K. Streubel, V. Härle, F. Scholz, M. Bode and M. Grundman, *J. Appl. Phys.* 71, 3300 (1992).
11. K.W. Cary, R. Hull, J.E. Fouquet, F.G. Kelleret and G.R. Trott, *Appl. Phys. Lett.* 51, 910 (1987).
12. R. Spycher, P.A. Buffat, P.A. Stadelmann, P. Roentgen, W. Heuberger and V. Graf, *Microsc. Semicond. Mater. Conf. 1989*, Inst. Phys. Conf. Ser. No. 100 (Inst. Phys., Bristol/London), p. 299.
13. R. Bhat, M.A. Koza, C.E. Zah, C. Caneau, C.C. Chang, S.A. Schwarz, A.S. Gozdz, P.S.D. Lin and A. Yi-Yan, *J. Cryst. Growth* 107, 871 (1991).
14. X.S. Jiang, A.R. Clawson and P.K.Y. Yu, *J. Cryst. Growth* 124, 547 (1992).
15. M.H. Lyons, E.G. Scott and M.A.G. Halliwell, *Microsc. Semicond. Mater. Conf. 1989*, Inst. Phys. Conf. Ser. No. 100 (Inst. Phys., Bristol/London), p. 473.
16. J. Hornstra and W.J. Bartels, *J. Cryst. Growth* 44, 513 (1978).