Evolution of Epilayer Tilt in Thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ Metamorphic Buffer Layers Grown by Hydride Vapor Phase Epitaxy

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Abstract

Tilt behavior in thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ metamorphic buffer layers (MBLs) grown by hydride vapor phase epitaxy (HVPE) was measured by high-resolution reciprocal space mapping. Step-graded and continuously-graded structures, grown on nominally (001) oriented GaAs substrates, were analyzed. Tilt was measured as a function of position in a step-graded MBL. It was found that the tilt was strongest near the edges and tended to point toward the sample center. Step-grading induced a nearly linear tilt increase with x_{InAs} , while tilt increased slowly below $x_{\text{InAs}} \sim 0.10$ then increased more sharply with In concentration in continuously-graded samples. The tilt behavior could be described by a model in which the tilt is attributed to imbalances in dislocations that result from cross-slip within a glide length of the sample edge. This finding implies that dislocation multiplication by cross slip is an important strain relief mechanism during the growth of these MBLs. Strategies for minimizing tilt in HVPE MBLs are discussed.

I. Introduction

Epitaxial layer tilt is commonly observed in the growth of strain-relaxed layers on lattice mismatched substrates. In III-V systems, strain relaxation usually occurs through the nucleation and glide of 60° misfit dislocations on $\{111\}$ planes [1]. The $\frac{a}{2} \langle 101 \rangle$ type burgers vectors of these dislocations are inclined 60° off their $[110]$ or $[\bar{1}10]$ line direction towards $[001]$ and can be resolved into 3 parts: $\langle 110 \rangle$ edge and screw components, and a $\langle 001 \rangle$ tilt component. The edge components relieve the misfit strain, while the screw components can create a twist about the interface if they are unbalanced. The tilt component, oriented normally to the (001) surface, creates a step on the layer surface while providing no strain relief. There are 8 slip systems that can be activated in the heteroepitaxy of III-V semiconductors [2]. While the misfit component of each burgers vector always has the same sign as dictated by the sign of the misfit [2], the sign of the out-of-plane component can vary, assuming a value of $[001]$ or $[00\bar{1}]$. If the nucleation of dislocations on these slip systems is sufficiently random, these components will cancel out, creating no net tilt. The surface orientation can tilt away from $[001]$ if dislocation populations are biased to a given slip system.

$\text{In}_x\text{Ga}_{1-x}\text{As}$ metamorphic buffer layers (MBLs) with tunable lattice constants can be used in device applications where a lattice parameter between GaAs and InP or between InP and InAs is desired. Recently they have garnered interest as a potential route to low strain mid-IR laser devices emitting in the 3.0-4.0 μm range [3, 4]. Growth of these devices is quite sensitive to the orientation of the substrate surface. The use of miscut substrates has been shown to cause ordering and roughening during the growth of strained balanced superlattice devices [5]. Tilt is regularly present in MBLs due to the fact that growth conditions which minimize threading dislocation densities promote relaxation by dislocation multiplication mechanisms which can also generate tilt [6]. Tilt in an MBL, while unintentional, can act as a miscut during device growth if the tilt is sufficiently large. Thus an understanding of the mechanisms controlling tilt in these layers is necessary to minimize adverse effects related to tilt.

In this study, the tilt in a number of thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ MBLs grown by hydride vapor phase epitaxy (HVPE) was measured by high resolution x-ray diffraction reciprocal space mapping. The tilt magnitude and direction as a function of depth in the sample were determined by this method. Tilt was measured as a function of position in one of the samples. Tilt in step- and continuously-graded structures was compared, and the effect of grading rate on tilting behavior was considered.

II. Experimental

$\text{In}_x\text{Ga}_{1-x}\text{As}$ metamorphic buffer layers were grown in an HVPE reactor by a process detailed previously [7]. The layers were deposited on GaAs substrates with a “nominally exact”, (001) $\pm 0.5^\circ$ orientation. Typically $\frac{1}{4}$ pieces of 2” wafers were used for growth. In one case, a 1 cm x 1 cm square piece cleaved along $\langle 110 \rangle$ edge directions was employed, to examine the effects of sample edges on tilt.

Two types of structures were grown: continuously-graded MBLs, in which the partial pressure of InCl (P_{InCl}) was increased at a constant rate during compositional grading, and step-graded MBLs, in which P_{InCl} was increased by a constant value at regular intervals up to the final composition. The growth rate typically decreased with increasing P_{InCl} , indicating that the growth was kinetically limited [3]. A thick, constant composition capping layer was grown at the final P_{InCl} after compositional grading by either method. Layer thicknesses were measured by scanning electron microscopy (SEM) in cross-section. The growth rate averaged $\sim 30 \mu\text{m/hr}$ at 740°C .

The samples were analyzed for composition, strain, and tilt by high resolution x-ray diffraction reciprocal space mapping (RSM). The employed triple crystal x-ray diffraction setup was comprised of a Cu $K\alpha$ source passed through a hybrid monochromator consisting of a closely coupled x-ray mirror and 4-bounce Ge (220) monochromator, with a 3-bounce Ge (220)

analyzer crystal placed after the sample. The beam was a line source, 12 mm tall, passed through a 1 mm wide slit. (004) and (115) reflections were utilized to determine the composition and strain of the final, thick capping layer in each sample. The relaxation of the intermediate steps was assumed to be nearly 100% as observed previously [3].

The tilt was obtained from the (004) RSM. Two RSMs were collected for each sample, with the beam direction aligned along $[110]$ and $[\bar{1}\bar{1}0]$ to obtain a complete description tilt vector. In step-graded samples, discrete reciprocal lattice points corresponding to each compositional step were mapped. By this method, a profile of the tilt as a function of composition and indirectly, depth, was obtained. The RSMs of the continuously-graded samples lacked discrete reciprocal lattice points, but the tilt was recorded at regular intervals between the substrate and capping layer to yield a tilt vs. composition (depth) profile.

III. Results

The first sample examined was a 10 step MBL grown on a 1 cm x 1 cm substrate (sample S0). Its growth parameters are listed in **Table 1**. The layer tilt in this sample was measured at 5 different positions using a Mo mask with a 3 x 3 mm square opening in order to determine the tilt variance as a function of position. The results of these measurements are presented in **Figure 1**. Note that the length of each vector represents the relative magnitude of the tilt. The positions of the measurements are approximate.

Figure 1 – Tilt magnitude and direction as a function of position for MBL1. Each tilt vector originates at the approximate position it was measured. The length of the vector represents its relative magnitude.

The tilt varied as a function of position in both direction and magnitude. Generally, the tilt at the sample edges tended to point away from the edges, inward towards the wafer center. The tilt was largest in the upper left portion of the sample, while it was the weakest in the middle. The magnitude was slightly larger towards the $[110]$ direction compared with $[\bar{1}\bar{1}0]$. A similar

pattern of tilts orthogonal to the sample edges was previously observed in graded $\text{In}_x\text{Ga}_{1-x}\text{As}$ buffer layers grown by MBE [8, 9].

Sample	Grading Style	T_D	x_{InAs} in Cap	Strain Grading Rate (μm^{-1})	Cap Thickness (μm)	Percent Relaxation (%)
S0	step	740 °C	0.33	0.0023	9	99
C1	continuous	740 °C	0.21	0.0012	10	89
C2	continuous	740 °C	0.28	0.0015	10	88
S1	step	740 °C	0.21	0.0015	10	96
S2	step	750 °C	0.30	0.0018	11	90

Table 1 – Growth parameters for the samples in this study.

A number of other MBL samples were grown to observe the effect of compositional grading style, strain rate, and final In composition on layer tilt. The growth parameters for these samples are also listed in **Table 1**. An S or C in the first position of the sample label indicates a step- or continuously-graded sample, respectively. The results presented for the subsequent samples were taken for a single position near the sample edge.

Figure 2 - Magnitude of the tilt vector as a function of x_{InAs} for the samples in this study.

The magnitude of the tilt vector is plotted as a function of composition in **Figure 2**. As all the samples were graded in the forward direction (x_{InAs} constantly increasing with thickness), making composition a proxy for depth.

The tilt increased monotonically with x_{InAs} for most of the samples. The magnitude of the tilt was always highest in the final capping layer. For a given capping layer composition, the use of continuous grading resulted in a smaller tilt (e.g., C1 vs. S1 and C2 vs. S2). The evolution of the tilt throughout the structure was slightly different depending on the grading style. Tilt in the

step-graded samples increased linearly with x_{InAs} . The slope of the tilt vs. x_{InAs} was larger for the step-graded sample with the higher grading rate (S1 vs. S2). For the continuously-graded samples, tilt increased slowly for $x_{\text{InAs}} < \sim 0.1$ and then increased more rapidly in continuously-graded samples. Both continuously-graded samples tilted to similar magnitudes as a function of x_{InAs} , despite having different grading rates.

IV. Discussion

There are multiple reports on mismatched epitaxial materials grown on exact-oriented (100) substrates that exhibit a tendency to tilt throughout the literature [10-13]. The finding that the tilt varied with position is consistent with the in previous reports on $\text{In}_x\text{Ga}_{1-x}\text{As}$ MBLs grown by MBE [8-10]. Whereas the positional variance in the findings of Kidd et al. [10] appeared random, the positional variance observed here tended to agree with that found by Natali et. al. [8], in which the tilt tended to be the strongest near sample edges, and point away from the edges towards the sample center.

The tilting in mismatched layers is related to the dislocation propagation mechanisms which operate in these layers to provide strain relief. Deposition of low defect density MBLs relies on the controlled introduction of strain over a given thickness. If the rate of strain introduction exceeds a certain threshold then 3D growth can result, accompanied by surface roughening, high defect nucleation rates, and high threading dislocation densities [10, 14]. A sufficiently low rate of strain introduction ensures that strain relaxation occurs by the operation of internal dislocation multiplication sources [14]. Multiplication is necessary because the substrate threading dislocation density (specified as $< 5000 \text{ cm}^{-2}$) would only be sufficient to relax a layer of $\text{In}_{0.003}\text{Ga}_{0.997}\text{As}$, assuming every threading dislocation formed a misfit dislocation in the heterointerface. Relaxation by multiplication mechanisms is desirable because long glide distances are promoted, resulting in increased annihilation of dislocation threading segments. Multiple Frank-Read type sources have been postulated and observed to operate [15-17]. These sources can develop by both dislocation pinning and cross slip [18].

Natali et. al. [8] described a mechanism by which tilt could be generated due to an imbalance of dislocation cross-slip near sample edges. They demonstrated that the tilt induced by a dislocation always points opposite the original propagation direction after cross-slip. In the middle of a sample, dislocations tend to glide from all directions, and the tilt induced by the individual dislocations tends to be balanced. Within a glide length of the sample edge, there must be an imbalance of cross-slipped dislocations from each direction since it is impossible for dislocations to glide in from beyond the sample edge. This imbalance leads to a pattern in which tilt is most pronounced near sample edges and points inward. Their model related the probability of a cross slip event to the inverse of the average glide length. The α glide length is almost 50x greater than the β glide length, based on GaAs dislocation velocities at 740 °C [19].

Thus more dislocations would be expected to cross slip from $\beta \rightarrow \alpha$, leading to stronger tilt they observed along $[110]$ vs. $[1\bar{1}0]$. This model would agree with our observations of the tilt in sample S0.

For this mechanism to operate in sample S0, however, the average dislocation glide length must be on the order of the sample dimensions. Assuming that each misfit dislocation possesses exactly 2 threading segments, the average glide length can be related to the threading dislocation density by:

$$L = \frac{4\delta}{\rho_{TD}|b|} \quad (1)$$

where δ is the amount of strain relieved, ρ_{TD} is the threading dislocation density, and $|b|$ is the magnitude of the misfit relieving component of the dislocation Burgers vector [20]. For a typical HVPE MBL with $x_{InAs} = 0.3$, $\delta \sim 0.020$ (assuming full relaxation) and $\rho_{TD} \sim 10^6 \text{ cm}^{-2}$ [7]. Assuming that the misfit dislocations are predominantly the 60° type [21], $|b| \sim 4 \times 10^{-8} \text{ cm}$ and the average glide length $L \sim 0.2 \text{ cm}$. The 4 measurements taken near the sample edges would fall within that range, with the sample center not much further away, indicating that this mechanism is a plausible explanation for the tilt in these samples. This model would account observation that the tilt tended to point inward in our samples and also that the strongest tilt occurs along the $[110]$ direction.

The tilt behavior was also controlled by the grading style. In a study on $\text{In}_x\text{Al}_{1-x}\text{As}$ buffer layers grown on (100) GaAs substrates by MBE, Lee et. al. [22] found that tilt increased more strongly with composition in step-graded layers when compared with continuously-graded layers, similar to results in the present study. The stronger tilting of the step-graded samples relative to the continuously-graded samples might be due the larger, discrete increases in strain during growth of the structure. A commonly cited mechanism is that threading dislocations in the most recent step can be turned over to form misfit dislocations at the interface between steps [23]. This mechanism would lead to lower overall threading dislocations by dislocation conservation. It would also provide a pathway by which tilt can propagate if these dislocations multiply in subsequent steps, as the Burgers vector sense would be preserved from step to step. Since discrete interfaces do not exist in the continuously-graded layers, the effect might not be as pronounced.

The results of this study indicate that there are multiple strategies available to minimize tilting in the MBL structure. The use of a large diameter substrate minimizes the amount of area which is within a glide length of the sample edge, mitigating the tilt caused by cross-slip mechanisms. Choices in the growth of the buffer layer also impact the tilt generation, as observed in this study. Use of continuous grading led to reduced tilt compared to step grading.

A smaller grading rate, which spreads out the strain over a larger thickness, can further reduce the tilt magnitude, regardless of whether step- or continuous-grading is employed.

V. Conclusions

The evolution of epilayer tilt in a number of thick HVPE $\text{In}_x\text{Ga}_{1-x}\text{As}$ MBLs grown by hydride vapor phase epitaxy (HVPE) was analyzed by x-ray reciprocal space mapping. On a given sample, the tilt was found to vary strongly in magnitude and direction as a function of position on the substrate. Tilt was strongest near the edges, with a direction pointing toward the sample center. Tilt typically increased steadily as a function of x_{InAs} regardless of grading style. Tilt in step-graded MBLs increased almost linearly with x_{InAs} while tilt in continuously-graded samples increased slowly $x_{\text{InAs}} < \sim 0.10$ then more rapidly above that threshold. The positional dependence of the tilt was explained by a model in which the majority of the dislocations are generated by cross-slip. Strategies for tilt minimization were outlined.

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References

- [1] J.W. Matthews, A.E. Blakeslee, Defects in epitaxial multilayers: I. Misfit dislocations, *Journal of Crystal Growth*, 27 (1974) 118-125.
- [2] J.E. Ayers, S.K. Ghandhi, L.J. Schowalter, Crystallographic tilting of heteroepitaxial layers, *Journal of Crystal Growth*, 113 (1991) 430-440.
- [3] K.L. Schulte, T.J. Garrod, T. Wan Kim, J. Kirch, S. Ruder, L.J. Mawst, T.F. Kuech, Metalorganic vapor phase growth of quantum well structures on thick metamorphic buffer layers grown by hydride vapor phase epitaxy, *Journal of Crystal Growth*, 370 (2013) 293-298.
- [4] L.J. Mawst, J.D. Kirch, T. Kim, T. Garrod, C. Boyle, D. Botez, B. Zutter, K. Schulte, T.F. Kuech, P.M. Bouzi, Low-strain, quantum-cascade-laser active regions grown on metamorphic buffer layers for emission in the 3.0-4.0 μm wavelength region, *Optoelectronics, IET*, 8 (2014) 25-32.
- [5] C. Giannini, L. Tapfer, Y. Zhuang, L. De Caro, T. Marschner, W. Stolz, Structural ordering and interface morphology in symmetrically strained $(\text{GaIn})\text{As}/\text{Ga}(\text{PAs})$ superlattices grown on off-oriented $\text{GaAs}(100)$, *Physical Review B*, 55 (1997) 5276-5283.
- [6] J. Tersoff, F.K. LeGoues, Competing relaxation mechanisms in strained layers, *Physical Review Letters*, 72 (1994) 3570-3573.
- [7] K.L. Schulte, B.T. Zutter, A.W. Wood, S.E. Babcock, T.F. Kuech, Design and characterization of thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ metamorphic buffer layers grown by hydride vapor phase epitaxy, *Semiconductor Science and Technology*, 29 (2014) 035013.
- [8] M. Natali, F. Romanato, E. Napolitani, D. De Salvador, A.V. Drigo, Lattice curvature generation in graded $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ buffer layers, *Physical Review B: Condensed Matter*, 62 (2000) 11054-11062.
- [9] F. Romanato, M. Natali, E. Napolitani, A.V. Drigo, A. Bosacchi, C. Ferrari, S. Franchi, G. Salviati, Lattice curvature of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ [001] graded buffer layers, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 16 (1998) 3578-3581.
- [10] P. Kidd, D.J. Dunstan, H.G. Colson, M.A. Loureno, A. Sacedon, F. Gonzalez-Sanz, L. Gonzalez, Y. Gonzalez, R. Garcia, D. Gonzalez, F.J. Pacheco, P.J. Goodhew, Comparison of the crystalline quality of step-graded and continuously graded InGaAs buffer layers, *Journal of Crystal Growth*, 169 (1996) 649-659.
- [11] J.M. Kang, C.S. Son, M.-S. Kim, Y. Kim, S.-K. Min, C.S. Kim, Origin of crystallographic tilt in $\text{InGaAs}/\text{GaAs}(001)$ heterostructure, *Applied Physics Letters*, 67 (1995) 641-643.
- [12] C. Ferrari, S. Gennari, S. Franchi, L. Lazzarini, M. Natali, F. Romanato, A.V. Drigo, J. Baruchel, Investigation by synchrotron radiation X-ray topography of lattice tilt formation in partially released $\text{InGaAs}/\text{GaAs}$ compositionally graded layers, *Journal of Crystal Growth*, 205 (1999) 474-480.
- [13] J.I. Chyi, J.L. Shieh, J.W. Pan, R.M. Lin, Material properties of compositional graded $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Al}_{1-x}\text{As}$ epilayers grown on GaAs substrates, *Journal of Applied Physics*, 79 (1996) 8367-8370.
- [14] P. Mooney, Strain relaxation and dislocations in SiGe/Si structures, *Materials Science and Engineering: R: Reports*, 17 (1996) 105-146.
- [15] R. Beanland, Dislocation multiplication mechanisms in low-misfit strained epitaxial layers, *Journal of Applied Physics*, 77 (1995) 6217-6222.
- [16] F.K. LeGoues, B.S. Meyerson, J.F. Morar, P.D. Kirchner, Mechanism and conditions for anomalous strain relaxation in graded thin films and superlattices, *Journal of Applied Physics*, 71 (1992) 4230-4243.
- [17] A. Lefebvre, C. Ulhaq-Bouillet, Multiplication of misfit dislocations in $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ heterostructures, *Philosophical Magazine A*, 70 (1994) 999-1012.
- [18] M.A. Capano, Multiplication of dislocations in $\text{Si}_{1-x}\text{Ge}_x$ layers on $\text{Si}(001)$, *Physical Review B*, 45 (1992) 11768.
- [19] I. Yonenaga, K. Sumino, Impurity effects on the generation, velocity, and immobilization of dislocations in GaAs , *Journal of Applied Physics*, 65 (1989) 85-92.

- [20] E.A. Fitzgerald, A.Y. Kim, M.T. Currie, T.A. Langdo, G. Taraschi, M.T. Bulsara, Dislocation dynamics in relaxed graded composition semiconductors, *Materials Science and Engineering: B*, 67 (1999) 53-61.
- [21] R. Beanland, D.J. Dunstan, P.J. Goodhew, Plastic relaxation and relaxed buffer layers for semiconductor epitaxy, *Advances in Physics*, 45 (1996) 87-146.
- [22] D. Lee, M.S. Park, Z. Tang, H. Luo, R. Beresford, C.R. Wie, Characterization of metamorphic $\text{In}_x\text{Al}_{1-x}\text{As}/\text{GaAs}$ buffer layers using reciprocal space mapping, *Journal of Applied Physics*, 101 (2007) 063523-063528.
- [23] M. Abrahams, L. Weisberg, C. Buiochi, J. Blanc, Dislocation morphology in graded heterojunctions: $\text{GaAs}_{1-x}\text{P}_x$, *Journal of Materials Science*, 4 (1969) 223-235.