Reduced dislocation density in $\text{Ga}_x\text{In}_{1-x}\text{P}$ compositionally graded buffer layers through engineered glide plane switch

K.L. Schulte*, R.M. France, W.E. McMahon, A.G. Norman, H.L. Guthrey, and J.F. Geisz

Abstract

In this work we develop control over dislocation glide dynamics in $\text{Ga}_x\text{In}_{1-x}\text{P}$ compositionally graded buffer layers (CGBs) through control of CuPt ordering of the group-III sublattice. The ordered structure is metastable in the bulk, so any glissile dislocation that disrupts the ordered pattern will release stored energy, and experience an increased glide force. Here we show how this connection between atomic ordering and dislocation glide force can be exploited to control the threading dislocation density (TDD) in $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs. When ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$ is graded from the GaAs to InP, the order parameter η decreases as x decreases, and dislocation glide switches from one set of glide planes to the other. This glide plane switch (GPS) is accompanied by the nucleation of dislocations on the new glide plane, which typically leads to increased TDD. We develop control of the GPS position within a $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGB through manipulation of deposition temperature, surfactant concentration, and strain-grading rate. We demonstrate a two-stage $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGB from GaAs to InP with sufficiently low TDD for high performance devices, such as the 4-junction inverted metamorphic multi-junction solar cell, achieved through careful control the GPS position. Experimental results are analyzed within the context of a model that considers the force balance on dislocations on the two competing glide planes as a function of the degree of ordering.

Keywords: A1. High resolution x-ray diffraction; A1. Line defects; A3. Metalorganic vapor phase epitaxy; B2. Semiconducting indium gallium phosphide; B3. Solar cells

1 Introduction

CuPt ordering of the group-III sublattice commonly develops during the epitaxial growth of ternary and quaternary III-V materials by metalorganic vapor phase epitaxy (MOVPE). This ordering induces changes in the optical, electronic, and structural properties of these materials [1]. Control over ordering is particularly important for optoelectronic devices such as LEDs, lasers, and multijunction solar cells because the emission and absorption change with the extent of the ordering, characterized by the order parameter, η [2]. Ordering has been well-studied in $\text{Ga}_x\text{In}_{1-x}\text{P}$, where it is induced by the surface reconstruction, and is therefore a function of numerous growth parameters, including substrate orientation, growth temperature, growth rate, V/III ratio, and surfactants [3, 4].

Ordering is important in the growth of lattice-mismatched materials, as it has been demonstrated that dislocation dynamics can be controlled to a large degree by the presence (or absence) of ordering [5, 6]. In most III-V alloys, the ordered configuration is metastable in the bulk, and energy can therefore be released by any

mechanism that disrupts the ordered configuration. The glide of dislocations that disrupt the ordered lattice are therefore energetically favored because they release stored energy by generating an anti-phase boundary (APB) in the ordered sublattice [5, 7]. The increase in glide force on APB-creating dislocations reduces the critical thickness at which glide occurs [8], potentially increasing glide lengths and reducing the residual threading dislocation density (TDD) of a compositionally graded buffer (CGB). The benefits of order-enhanced glide can be exploited by choosing growth conditions that induce a high degree of ordering as a means to limit TDD during the growth of CGBs.

$\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs are typically grown on (001) GaAs substrates with a small B-miscut towards the $[\bar{1}11]$ direction, which induces single-variant ordering on alternating $(\bar{1}11)$ planes (referred to hereafter as 'B-'), as shown in Fig. 1. Growth of GaInP on substrates with A-miscuts is known to induce multi-variant ordering and significant phase separation, and is thus typically avoided [9]. The B-miscut leads to a larger resolved shear stress on the $(\bar{1}11)$ plane, which normally would favor dislocation nucleation and glide on that plane [10-12]. The presence of ordering enhances glide on $(1\bar{1}1)$ planes (referred to hereafter as 'B+'), however, since dislocations that glide on B+ planes disrupt the order pattern. The force balance between glide on B- and B+ is controlled through the order parameter, strain, and substrate miscut, and dislocations have been observed to predominantly glide on the B+ planes when the order parameter is high [5].

The maximum achievable order parameter is determined by the composition. It is highest for a highly mixed ternary such as $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, and lowest for a binary such as InP, where (due to the absence of Ga), $\eta = 0$. In compressive $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs on GaAs that alter the lattice constant from $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ to InP, the order parameter necessarily decreases during growth (as depicted in Fig. 1). Glide on B+ planes is more favored early in the CGB growth when the $\text{Ga}_x\text{In}_{1-x}\text{P}$ composition is closer to $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and the order parameter can be higher. Closer to InP, the driving force for B+ glide dissipates and the force on the B- dislocations, due to the higher resolved shear misfit stress, becomes higher than that on B+ dislocations. At some intermediate point in the grade, a "glide plane switch" (GPS) from B+ glide to B- glide occurs. If insufficient dislocations exist with Burgers vectors on the B- plane, the GPS must occur in part by nucleation of new dislocations, since cross slip of strain-relieving TDs from B+ to B- is forbidden because the Burgers vector for any given glissile strain-relieving dislocation lies within either the B+ plane or the B- plane, but not both [13].

The ability to control the influence of atomic ordering on glide, and induce GPS on command would be a useful tool in the growth of metamorphic materials. For instance, the 4-junction inverted metamorphic solar cell (4JIMM) uses a 2-stage $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade from GaAs to InP that pauses at $\text{Ga}_{0.26}\text{In}_{0.74}\text{P}$ for growth of the 1.0 eV GaInAs cell and then restarts to finish grading to the InP. A GPS occurs at roughly $\text{Ga}_{0.15}\text{In}_{0.85}\text{P}$, which is close to the InP lattice constant at which the 4th junction is

grown [14]. In practice, the grade rate is reduced by 50% just before this composition in order to minimize dislocation interaction and TDD, which enables metamorphic cells with high V_{OC} , but adds increased thickness and cost to the device. If the GPS could be engineered to occur in a less critical region of the device, for example, when the grade restarts immediately after growth of the 3rd junction, it might be possible to suppress the TDD without thickening.

The present study will develop control of the GPS through manipulation of key parameters that control ordering. Previously, the effects of substrate miscut and Sb surfactant on the glide plane distribution and GPS position have been demonstrated [5, 6, 15]. In this study, the effects of growth temperature, grading rate, and the use of a Se surfactant on the GPS position will be demonstrated. The experimental results will be evaluated in context of the force balance model for strain relaxation in the presence of ordering. GPS control will be used to develop two-stage $Ga_xIn_{1-x}P$ CGBs to InP in which the GPS is placed within or at the start of the second stage. The utility of GPS control will be demonstrated through the reduced TDD of the latter structure.

2 Experimental

$Ga_{0.5}In_{0.5}P$ epilayers and $Ga_xIn_{1-x}P$ compositionally graded buffer layers were grown by atmospheric pressure MOVPE using trimethylgallium, trimethylindium, and phosphine. Doping was achieved using dimethylzinc, disilane, and hydrogen selenide. All structures were grown on Si-doped, n+ (001) GaAs miscut 2° towards (111)B. The standard CGB structure employed here, unless noted otherwise, was described in ref [14]. Briefly, a lattice matched $Ga_{0.505}In_{0.495}P$ epilayer was grown, and then the $Ga_xIn_{1-x}P$ was graded to $Ga_{0.20}In_{0.80}P$ with a strain rate of 1%/μm using 250 nm compositional steps. From $Ga_{0.20}In_{0.80}P$ to InP, the strain rate was 0.5%/μm and 125 nm steps were used. At the end of the grade, a thick 1.5 μm InP capping layer was grown. Curvature in both the [110] and $[\bar{1}10]$ directions was measured *in situ* in multi-beam optical stress sensor (MOSS) with a 3 x 3 laser spot array as in ref. [15, 16]. Electron beam induced current (EBIC) images were obtained from select samples, using a scanning electron microscope with excitation voltages between 5-15 kV. $4 \times 10^{-4} \text{ cm}^2$ area or more was analyzed for each sample.

Reciprocal space maps (RSM) of the (004), (115), and (224) reflections were measured by high-resolution x-ray diffraction in order to obtain information about the composition, relaxation, and tilt of the CGBs. A Cu Kα source was refined using a hybrid monochromator consisting of closely coupled parabolic x-ray mirror and four bounce Ge 004 monochromator. An open, large area pixelated detector permitted spatial analysis of the diffracted radiation without the need for refinement using an analyzer crystal. Relaxation in the final capping layer was usually close to 100% [14]. RSMs were plotted with the Omega-2Theta angle in the vertical direction, and the Omega angle in the horizontal direction.

(004) RSMs obtained with the plane of the diffractometer aligned along $[\bar{1}11]$ are of

particular interest in this study (and are the only RSMs plotted hereafter), since the miscut and ordering are both aligned along this direction. Relaxation in graded III-V materials occurs through the glide of 60° dislocations on $\{111\}$ family planes with $\frac{a}{2} < 101 >$ type burgers vectors [17]. Dislocations aligned in the same direction on opposite glide planes (B- vs. B+, for example) possess burgers vectors with the same misfit component but opposite tilt components. The tilt components will cancel out as long as the dislocations are distributed equally on the opposite glide planes [10, 11]. An imbalance of glide on one glide plane or the other will manifest as a tilt towards or away from $[001]$. Deviation away from $\Omega = 0$ along the x-axis of (004) RSMs can only be due to epilayer tilt. Thus (004) RSMs provide a direct probe of the extent of relaxation occurring on the B+ vs. B- planes and, by extension, the forces acting on these dislocations. In the RSMs presented in this study, positive tilt on the Ω axis is related to relaxation on the B+ plane, which is favored by the presence of ordering (as in Fig. 1). Negative tilt on the Ω axis is related to relaxation on the B- plane, which is favored by the higher resolved shear stress imparted on that plane due to the miscut. The dislocation distribution at a given point in a grade can be calculated from the magnitude and direction of the tilt by [6]:

(1)

$$P_{(\bar{1}11)} = \frac{1}{2} \left(1 + \frac{\tan \alpha_{[110]}}{\sqrt{2}\Delta\epsilon} \right)$$

where $P_{(\bar{1}11)}$ is the percentage of glide which occurred on the $(\bar{1}11)$ or B- plane, $\alpha_{[110]}$ is the tilt angle around the $[110]$ axis, and $\Delta\epsilon$ is the amount of strain relieved. $\alpha_{[110]}$ is defined as positive for tilt away from the surface normal. This analysis assumes that 100% strain relaxation.

The tilt around the $[\bar{1}11]$ axis was typically negligible, indicating a balanced distribution of α , or $[\bar{1}11]$ aligned, dislocations. These dislocations will not be considered further.

3 Results and Discussion

The force balance model used in this study was developed in ref [5]. The order parameter at which the GPS is expected to occur was evaluated by calculating the forces acting on dislocations in each plane and solving for the value of η at which these forces balance exactly. The result of this analysis yields Eq. (2), where η_{GPS} is the order parameter at glide plane switch, M is the biaxial modulus, ϵ is the in-plane strain, E_{APB}^{max} is the energy released by generation of an APB through dislocation glide on the B+ plane, a_0 is the relaxed lattice constant, β is the angle between (001) and each glide plane (54.74° for $\{111\}$ planes), and δ is the angle of substrate miscut off (001).

(2)

$$\eta_{gps} = \sqrt{\frac{M \cdot |\epsilon|}{E_{APB}^{max}} \cdot \frac{\sqrt{3}}{2\sqrt{2}} a_0 \cdot \cos(2\beta) \cdot \sin(2\delta)}$$

GPS occurs when the order parameter at the growth surface drops below η_{GPS} . For a given alloy, GPS can be induced in two ways: either by reducing the order parameter of the growing crystal such that it drops below η_{GPS} , or modifying the right side of Eq. (2) to increase η_{GPS} . The former can be accomplished by varying parameters like deposition temperature, growth rate, or using surfactants, while the latter is accomplished by increasing the miscut δ [5], or, as will be demonstrated, changing the grading rate to modify ϵ . The following results are organized according to the parameter that was varied, and analyzed in context of this model.

3.1 Effect of Deposition Temperature

We first evaluated the order parameter of a series of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ epilayers grown on GaAs at varying deposition temperatures to build a basis for understanding the effect of this parameter on GPS. The order parameter can be readily determined from lattice-matched epilayers through measurement of strain anisotropy that develops as a result of ordering using MOSS [15]. The ordered epilayer exhibits a rhombohedral distortion, lengthening along the $[\bar{1}10]$ direction normal to the ordered planes and shrinking along $[110]$. The magnitude of strain anisotropy was measured by MOSS and then the order parameter was determined using the relation $\Delta\epsilon_{MOSS} = \Delta\epsilon_{MAX} \cdot \eta^2$, where $\Delta\epsilon_{MOSS}$ is the measured strain anisotropy, $\Delta\epsilon_{MAX}$ is the anisotropy of a perfectly ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ epilayer obtained from DFT calculations, equal to 0.27% [15]. There is some uncertainty in the precise determination of η by this method, but we observed a strong trend in $\Delta\epsilon_{MOSS}$ as a function of temperature and have confidence in the internal consistency of the data.

The MOSS order parameter as a function deposition temperature in the range 580-675 °C is plotted in Fig. 2. The order parameter increased monotonically with temperature in this range, possibly due to improved surface diffusion at higher temperature, which allowed more of the surface to attain a reconstruction conducive to ordering. This effect was particularly strong at the lower end of the range, with the order parameter increasing from nearly 0.07 at 580 °C to 0.27 at 595 °C. The order parameter then started to plateau, increasing by only 0.2 over the last 80 °C of the tested range.

Next, we grew a series of $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs from GaAs to InP using the standard structure described in Section 2, in which the temperature was varied at a specific point in the grade (this structure is shown in Fig. 3). The growth temperature was held constant at 675 °C from $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ to $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ in all structures, and then constant at another temperature in the range 580-675 °C for the $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ to InP portion of the grade. The temperatures of the second stage of the grade were chosen to match the temperatures of the epilayers grown for the analysis of Fig. 2.

(004) reciprocal space maps of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs are plotted in Fig. 3. All samples exhibited glide predominantly on the B+ plane in the beginning portion of the grade grown at 675 °C, as indicated by the positive Omega tilt. A GPS to the B- plane occurred later in the grade for all samples, as indicated by a tilt back towards Omega = 0. The GPS occurred earlier with decreasing temperature, with the effect becoming strongest in the 595 °C and 580 °C samples. This coincided with the trend in order parameter measured in the epilayers in Fig. 2. The sharpest change in η was observed between 595 °C and 580 °C in the epilayers, and this trend was replicated in the graded buffers. GPS occurred slightly earlier with decreasing temperature in the CGBs grown between 675 °C and 595 °C but strongest GPS occurred in the 580 °C sample, in which GPS initiated immediately as the temperature was reduced from 675 °C.

We can predict the expected GPS composition using the force balance model and the order parameters calculated from the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ epilayers. If we assume ϵ and the various materials properties are constant with temperature in this range, the right side of Eq. (2), and η_{GPS} , is constant for all of these samples. By using the relation:

(3)

$$\eta(x) = \eta(0.5) \cdot 2x [5],$$

where x is the fraction of Ga in $\text{Ga}_x\text{In}_{1-x}\text{P}$, we can calculate the expected composition at GPS as a function of deposition temperature by substituting η_{GPS} calculated from Eq. 2 for $\eta(x)$, and solving for x as a function of temperature using the values of $\eta(0.5)$ measured in the epilayers of Fig. 1. Note that, in this analysis, we are assuming that the lattice mismatched relative order parameter is equal to the lattice matched relative order parameter.

Figure 4 shows the calculated GPS concentration as a function of temperature for multiple ϵ , since we were not able to determine that parameter experimentally. The GPS concentration determined experimentally from the RSMs of Fig. 3 are also plotted as a function of temperature. The 580 °C sample was omitted, since GPS occurred immediately as the temperature was decreased from 675 °C. Thus the true GPS composition for that sample is unknown. We observe good agreement between the experiment and the model, which replicates the general trend in the data. The best fit occurs for a $\epsilon = -0.0023$, which is reasonable for these growth conditions.

3.2 Effect of Se Surfactant

Another way to reduce the order parameter is through the use of surfactants, which can modify the surface reconstruction and suppress the formation of ordering which would normally be stabilized by the surface. Sb and Se are commonly known to act as surfactants in the growth of many III-V materials by MOVPE [15, 18-21]. The use of Se is particularly attractive in the growth of CGBs for applications where increased transparency is required in the buffer. Highly degenerate n-type doping is readily obtainable with Se, which leads to blue shifting of the absorption edge of the

CGB (and InP cap) through the Burstein-Moss effect [21]. High quality, highly transparent $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs to InP with degenerate Se doping for solar applications have already been demonstrated [22]. The surfactant effect of the Se on order enhanced dislocation glide in the CGB will be considered here.

We deposited two $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs with Se doping turned on at different positions in the grade to test the effectiveness of Se in controlling the order parameter. Each CGB was doped $\sim 1 \times 10^{19} \text{ cm}^{-3}$ with H_2Se flow turned on at $\text{Ga}_{0.1}\text{In}_{0.9}\text{P}$ and $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$, respectively. The growth temperature was 675°C . Figure 5 presents (004) reciprocal space maps for these Se-doped CGBs. Initially, relaxation was dominated by glide on the B+ planes in both samples, which is favored by the presence of ordering. In each case, GPS occurred as soon as the H_2Se flow was initiated. η_{GPS} calculated from the model is ~ 0.1 under these growth conditions, and the order parameter of $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ under these growth conditions is estimated from the epilayer data to be 0.2. Thus, to induce GPS, the $\sim 1 \times 10^{19} \text{ cm}^{-3}$ Se doping has reduced η by at least 0.1 in that case.

3.3 Effect of Strain Rate

While GPS was induced in the previous sections by reducing η to a value below η_{GPS} , it is also possible to modify η_{GPS} itself by modulating parameters on the right side of Eq. 1. Given a specific alloy system with fixed materials constants, we can modify η_{GPS} through either the miscut angle (δ) or the in-plane strain (ϵ). The effect of miscut angle on glide has been explored previously [5]. The in-plane strain cannot be controlled directly, but can be modified through the strain rate. All relaxing materials contain a small but significant in-plane strain at the surface and, in compositionally graded buffer layers, this strain is proportional to the strain-grading rate [23, 24]. Employment of a high strain-grading rate offers the benefit of reduced growth time and materials usage, provided that TDD can be controlled to a reasonable level.

We grew a series of $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs with varying strain rate to test the effect of the strain rate on the GPS position. Four samples were grown with two constant strain rate stages. In the first stage, from $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ and $\text{Ga}_{0.1}\text{In}_{0.9}\text{P}$, the strain rate was set between $1\%/ \mu\text{m}$ and $2.5\%/ \mu\text{m}$. In the second stage, from $\text{Ga}_{0.10}\text{In}_{0.90}\text{P}$ to InP, the strain rate was of $0.5\%/ \mu\text{m}$ in all samples. The structure and RSM data for this set of samples are shown in Fig. 6. Note that in the RSM plots, the center of a fit to the intensity as a function of Omega is plotted for each value of Omega-2Theta in order to compare multiple RSMs on the same graph. The GaP concentration (in $\text{Ga}_x\text{In}_{1-x}\text{P}$) at GPS is plotted on the left axis of Fig. 7.

The GPS concentration varied strongly with the grading rate, increasing from $x_{\text{GaP}} = 0.13$ to 0.26 as the strain grading rate was increased from $1.0\%/ \mu\text{m}$ to $2.5\%/ \mu\text{m}$. The final tilt in the InP cap at the end of the grade also decreased strongly with strain rate as a consequence of the GPS occurring earlier in the grade. We can use

Eqs. (2) and (3) to estimate the in-plane strain at the growth surface, ϵ , as a function of the strain rate. The order parameter at GPS, η_{GPS} , can be calculated by inserting the GaP concentration (x) at GPS for each strain rate into Eq. 3. η_{GPS} is then equated with the right side of Eq. (2), which can be rearranged to solve for ϵ . The results of this calculation are plotted as a function of strain grading rate on the right axis of Fig. 7.

The calculated magnitude of in-plane strain was 0.0025 for a strain rate 1.0%/μm. This value agrees with in-plane strain estimated from the GPS vs. temperature relationship determined in Fig. 4. ϵ increased in a superlinear fashion with strain rate, reaching a value of 0.0100 at 2.5%/μm. Tersoff's equilibrium model for the dislocation distribution in a linearly graded buffer predicted a square root dependence of the in-plane strain at the surface on the strain rate [23]. This contrasts slightly with our observation that the strain exhibited a super-linear dependence on strain rate. Dislocation interactions, which were neglected in Tersoff's model, might be playing a role, however, since a higher strain rate forces misfit dislocations (and associated threads) to be confined closer together in a smaller space. This could limit dislocation glide lengths and overall relaxation, resulting in the larger residual strains than are predicted by the equilibrium model.

3.4 Engineering the GPS in a Compositionally Graded Buffer

The ability to actively control the order parameter during the growth of mismatched materials enables the development of graded buffers with an engineered GPS. Through careful growth design, the GPS can be placed in regions of the grade that potentially minimize its impact on TDD and device performance. A specific application where GPS engineering would be beneficial is in inverted metamorphic multi-junction (4JIMM) solar cells. The first two junctions of the 4JIMM cell [25] consist of $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ (1.9 eV) and GaAs (1.4 eV) cells lattice-matched to GaAs. After growth of the GaAs cell, a $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade to $\text{Ga}_{0.26}\text{In}_{0.74}\text{P}$ is grown, and then a mismatched $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ (1.0 eV) cell is grown. Another $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade is grown, this time to InP, and a $\text{Ga}_{0.46}\text{In}_{0.54}\text{As}$ (0.7 eV) cell is grown as the 4th and final junction. Under typical growth conditions, the GPS occurs just after $\text{Ga}_{0.15}\text{In}_{0.85}\text{P}$, and leads to an elevated TDD in the 4th cell. Consequently, this cell is the limiting factor in the performance of the IMM device [26]. The performance of this junction can be improved by reducing the strain grading rate near the GPS [14], but this thickens the buffer significantly, leading to higher growth time, greater materials consumption, and higher costs. The strain grading rate is typically reduced from 1.0%/μm to 0.5%/μm in the 4JIMM to obtain a graded buffer of sufficient quality. Engineering the GPS such that it occurs in a different region of the device could allow thinning of the buffer while maintaining device performance, leading to reduced costs.

One potential position for the GPS is immediately after growth of the $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ 1.0 eV cell after which the second stage of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade begins. If dislocation nucleation and glide could be induced on the B- plane instead of the B+ plane at this point, the GPS would no longer occur in the middle of the second stage, after

dislocations have already been nucleated on the B+ plane. To test this theory, a series of three $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs to InP was grown with a 3 μm thick isotype $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ layer inserted halfway through the grade to InP, as shown in Fig. 8. The isotype layer was preceded by a 1 μm thick $\text{Ga}_{0.23}\text{In}_{0.77}\text{P}$ strain overshoot layer and a 1 μm $\text{Ga}_{0.26}\text{In}_{0.74}\text{P}$ cap layer. A 1.5 μm InP cap was grown at the end of the second stage of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade. The entire structure was doped n-type except for the last 0.2 μm of the InP cap, which was doped p-type to create a pn junction for EBIC measurements. This structure is analogous to the 4JIMM, but without the 0.7 eV GaInAs cell so that the final dislocation density in the graded buffer can be analyzed. The growth temperature was 675 °C and the grading rate was 1% strain/ μm in both stages of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ grade, making the second stage of the buffer roughly half as thick as the buffer used in refs. [14] and [25]. The GPS was allowed to occur naturally in a control sample, and two samples with engineered GPS position were also grown. In one sample, Sample A, GPS was induced using a reduced temperature of 580 °C in the second stage of the GaInP grade. In the other sample, Sample B, Se was turned on at the start of the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage to induce GPS, while the growth temperature remained 675 °C throughout the whole structure.

Figure 8 shows reciprocal space maps of the Control, Sample A, and Sample B. EBIC images of each sample are shown in Figure 9. The percentage of relaxation on each plane, B+ ($1\bar{1}1$) vs. B- ($\bar{1}11$) was calculated at specific points in the grade using Eq. (1). The percentage of glide on the B+ plane at the end of the first stage and at the start of the second stage as well as the TDD measured at the InP surface are listed for each sample in Table 1.

At least 95% of dislocation glide occurred on the B+ plane in the first $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage in all 3 samples, due to the high degree of ordering present in that stage. In the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage of the control sample, relaxation was again controlled predominantly by ordering, with 79% of glide occurring on the B+ plane. A typical GPS occurred just before the growth of the InP cap layer at $\sim\text{Ga}_{0.10}\text{In}_{0.90}\text{P}$. After the GPS, only 36% of the glide was on the B+ plane.

In Sample A, reducing the temperature to 580 °C for the growth of the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage in Sample A caused a majority of relaxation in that stage to occur on the B- plane. Overall, the relaxation is relatively balanced between the B+ and B- planes (46% vs. 54%), however. Glide did not fully transition to the B- plane until around -4000 arc seconds, roughly $\text{Ga}_{0.10}\text{In}_{0.90}\text{P}$, implying that new dislocations nucleated at that position graded buffer. Since B- glide predominated over more of the grade, the overall tilt of the InP cap was smaller than in the control. The FWHM of the cap was much higher than in the control.

Use of surfactants in sample B during the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage led to a much stronger GPS at resumption of the grade, with only 33% of glide occurring on the B+ plane. The FWHM of the InP cap was 1100 arc seconds, which was lower than even the control sample.

The Control and Sample A have a similar TDD of $\sim 1 \times 10^7 \text{ cm}^2$. Sample B, which did not have a GPS within the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage and the highest percentage of glide on the B- plane in that stage, had a TDD which was less than half the TDD of Sample A and the Control. An increase of 50 mV in the V_{OC} in GaAs cells on mismatched substrates was demonstrated previously for that level of TDD reduction [27]. Furthermore, this TDD is equivalent to that obtained in $\text{Ga}_x\text{In}_{1-x}\text{P}$ grades grown without GPS engineering but that are thickened near the GPS [14]. Elimination of buffer thickening results in a reduction of 25% in total buffer thickness while maintaining a similar TDD. This result demonstrates the utility of control of the dislocation dynamics during the growth of mismatched materials.

4 Conclusions

Precise control over dislocation glide plane switch was demonstrated in $\text{Ga}_x\text{In}_{1-x}\text{P}$ compositionally graded buffer layers from the GaAs to InP lattice constants. The effects of growth temperature, use of Se as a surfactant, and strain-grading rate on atomic ordering and dislocation distributions in the CGBs were explored and analyzed in the context of a force balance model. Growth temperatures below 600 °C were required to significantly reduce ordering, and a temperature of 580 °C was necessary to induce instantaneous GPS. Limited control over GPS was exerted through manipulation of the strain-grading rate, though this technique is limited by the fact that TDD tends to increase with strain rate. Se, used at concentrations which led to $\sim 1 \times 10^{19} \text{ cm}^{-3}$ doping level, induced GPS as soon as Se flow was turned on. Strategic placement of the GPS in a two-stage $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGB to InP was demonstrated through the use of reduced temperature or Se in the second stage of the grade. Se was more effective than reduced growth temperature at inducing GPS to the B- glide plane. Significant TDD reduction was demonstrated in the Se doped structure compared to a control sample grown at 675 °C without surfactants, highlighting the utility of the ability to control dislocation dynamics during the growth of mismatched materials.

Acknowledgments

The authors would like to thank Michelle Young for device processing and Waldo Olavarria for materials growth. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08G028308 with the National Renewable Energy Laboratory. Funding provided by U.S. DOE Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Program.

The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

References

- [1] A. Mascarenhas, Y. Zhang, The Physics of Tunable Disorder in Semiconductor Alloys, in: Spontaneous Ordering in Semiconductor Alloys, Springer, 2002, pp. 283-326.
- [2] R. Forrest, T. Golding, S. Moss, Y. Zhang, J. Geisz, J. Olson, A. Mascarenhas, P. Ernst, C. Geng, X-ray diffraction and excitation photoluminescence analysis of ordered GaInP, Physical Review B, 58 (1998) 15355.
- [3] G. Stringfellow, Effects of the surface on CuPt ordering during OMVPE growth, in: Spontaneous Ordering in Semiconductor Alloys, Springer, 2002, pp. 99-117.
- [4] T. Suzuki, A. Gomyo, S. Iijima, Strong ordering in GaInP alloy semiconductors; Formation mechanism for the ordered phase, Journal of Crystal Growth, 93 (1988) 396-405.
- [5] W.E. McMahon, J. Kang, R.M. France, A.G. Norman, D.J. Friedman, S.-H. Wei, Ordering-enhanced dislocation glide in III-V alloys, Journal of Applied Physics, 114 (2013) 203506.
- [6] R.M. France, W.E. McMahon, A.G. Norman, J.F. Geisz, M.J. Romero, Control of misfit dislocation glide plane distribution during strain relaxation of CuPt-ordered GaInAs and GaInP, Journal of Applied Physics, 112 (2012) 023520-023526.
- [7] E. Spiecker, M. Seibt, W. Schröter, R. Winterhoff, F. Scholz, Exploiting long-range atomic ordering for the investigation of strain relaxation in lattice-mismatched epitaxy: A case study on CuPtB-type ordered (GaIn) P on GaAs, Applied Surface Science, 188 (2002) 61-68.
- [8] R.M. France, W.E. McMahon, H.L. Guthrey, Critical thickness of atomically ordered III-V alloys, Applied Physics Letters, 107 (2015) 151903.
- [9] R.M. France, Dislocation formation and glide in atomically-ordered III-V semiconductors, in, Colorado School of Mines, 2015.
- [10] P.M. Mooney, F.K. LeGoues, J. Tersoff, J.O. Chu, Nucleation of dislocations in SiGe layers grown on (001)Si, Journal of Applied Physics, 75 (1994) 3968-3977.
- [11] J.E. Ayers, S.K. Ghandhi, L.J. Schowalter, Crystallographic tilting of heteroepitaxial layers, Journal of Crystal Growth, 113 (1991) 430-440.
- [12] F. Riesz, Crystallographic tilting in lattice-mismatched heteroepitaxy: A Dodson--Tsao relaxation approach, Journal of Applied Physics, 79 (1996) 4111-4117.
- [13] D. Hull, D.J. Bacon, Introduction to dislocations, Elsevier, 2011.
- [14] R.M. France, I. García, W.E. McMahon, A.G. Norman, J. Simon, J.F. Geisz, D.J. Friedman, M.J. Romero, Lattice-mismatched 0.7-eV GaInAs solar cells grown on GaAs using GaInP compositionally graded buffers, IEEE Journal of Photovoltaics, 4 (2014) 190-195.
- [15] R.M. France, W.E. McMahon, J. Kang, M.A. Steiner, J.F. Geisz, In situ measurement of CuPt alloy ordering using strain anisotropy, Journal of Applied Physics, 115 (2014) 053502.
- [16] J. Geisz, A. Levander, A. Norman, K. Jones, M. Romero, In situ stress measurement for MOVPE growth of high efficiency lattice-mismatched solar cells, Journal of Crystal Growth, 310 (2008) 2339-2344.
- [17] J.W. Matthews, A.E. Blakeslee, Defects in epitaxial multilayers: I. Misfit dislocations, Journal of Crystal Growth, 27 (1974) 118-125.

- [18] J. Kirch, T.W. Kim, J. Konen, L.J. Mawst, T.F. Kuech, T.S. Kuan, Effects of antimony (Sb) incorporation on MOVPE grown $\text{InAs}_y\text{P}_{1-y}$ metamorphic buffer layers on InP substrates, *Journal of Crystal Growth*, 315 (2011) 96-101.
- [19] C. Fetzer, R. Lee, J. Shurtleff, G. Stringfellow, S. Lee, T.Y. Seong, The use of a surfactant (Sb) to induce triple period ordering in GaInP, *Applied Physics Letters*, 76 (2000) 1440-1442.
- [20] A. Gomyo, H. Hotta, I. Hino, S. Kawata, K. Kobayashi, T. Suzuki, Silicon and selenium doping effects on band-gap energy and sublattice ordering in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ grown by metalorganic vapor phase epitaxy, *Japanese Journal of Applied Physics*, 28 (1989) L1330.
- [21] S.R. Kurtz, J. Olson, J. Goral, A. Kibbler, E. Beck, The effect of selenium doping on the optical and structural properties of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, *Journal of Electronic Materials*, 19 (1990) 825-828.
- [22] K.L. Schulte, R.M. France, J.F. Geisz, in review, *IEEE Journal of Photovoltaics*, (2016).
- [23] J. Tersoff, Dislocations and strain relief in compositionally graded layers, *Applied Physics Letters*, 62 (1993) 693-695.
- [24] R. Beanland, D.J. Dunstan, P.J. Goodhew, Plastic relaxation and relaxed buffer layers for semiconductor epitaxy, *Advances in Physics*, 45 (1996) 87-146.
- [25] R.M. France, J.F. Geisz, I. García, M.A. Steiner, W.E. McMahon, D.J. Friedman, T.E. Moriarty, C. Osterwald, J.S. Ward, A. Duda, Quadruple-junction inverted metamorphic concentrator devices, *IEEE Journal of Photovoltaics*, 5 (2015) 432-437.
- [26] I. Garcia, R.M. France, J.F. Geisz, W.E. McMahon, M.A. Steiner, S. Johnston, D.J. Friedman, Metamorphic III-V Solar Cells: Recent Progress and Potential, *IEEE Journal of Photovoltaics*, 6 (2016) 366-373.
- [27] C.L. Andre, III-V semiconductors on SiGe substrates for multi-junction photovoltaics, in, *The Ohio State University*, 2004.

Figure 1 – Illustration of dislocation glide in ordered GaInP grown on a GaAs substrate miscut 2° towards $[\bar{1}11]$. Dislocations that glide on $(\bar{1}\bar{1}1)$, or B- planes, preserve the ordered lattice configuration while dislocations gliding on $(1\bar{1}1)$, or B+ planes, introduce anti-phase disorder onto the ordered sub-lattice. B+ glide is favored when ordering is high, while B- glide is favored by an increased shear stress due to the miscut. The (004) reciprocal space maps of representative compositionally graded buffers (CGBs) are sensitive to glide on specific glide planes, which manifests as tilt. A negative tilt occurs when relaxation predominantly occurs on B- planes, with the epilayer tilting towards the surface normal. A positive tilt occurs when relaxation predominates on B+ planes, with the epilayer tilting away from the surface normal. As the CGB is graded from $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ towards InP , order is constantly decreasing.

Figure 2 – Order parameter of lattice matched $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ as a function of deposition temperature as determined by strain anisotropy measurement using a multi-beam optical stress sensor (MOSS).

Figure 3 – (004) reciprocal space maps for a series of $\text{Ga}_x\text{In}_{1-x}\text{P}$ grades from GaAs to InP with varied growth temperatures. The growth temperature was held constant at 675 °C from $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ to $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ in all structures, and then constant at another temperature in the range 580-675 °C for the $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ to InP portion of the grade.

Figure 4 – Calculated GaP composition (in $\text{Ga}_x\text{In}_{1-x}\text{P}$) at GPS as a function of temperature. The experimentally determined GPS composition for a series $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs is plotted with the red markers.

Figure 5 – (004) reciprocal space maps of $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs grown with Se flow turned on at $\text{Ga}_{0.1}\text{In}_{0.9}\text{P}$ (top) and $\text{Ga}_{0.2}\text{In}_{0.8}\text{P}$ (bottom).

Figure 6 – (left) $\text{Ga}_x\text{In}_{1-x}\text{P}$ graded buffer structure with varied strain rate between $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ and $\text{Ga}_{0.1}\text{In}_{0.9}\text{P}$ and a $0.5\%/ \mu\text{m}$ strain rate from $\text{Ga}_{0.1}\text{In}_{0.90}\text{P}$ to InP . (right) Omega tilt as a function of Omega-2Theta for this series of samples.

Figure 7 – Left axis: GaP concentration (in $\text{Ga}_x\text{In}_{1-x}\text{P}$) at GPS as a function of strain grading rate. Right axis: in-plane strain calculated from Eq. (2) using the experimentally determined GPS concentration.

Fig. 8 – (004) RSMs for a series of $\text{Ga}_x\text{In}_{1-x}\text{P}$ CGBs to InP with a $3\ \mu\text{m}$ thick $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ layer inserted halfway through the grade. A control sample was grown, with a growth temperature of $675\ ^\circ\text{C}$ throughout the entire grade and without surfactants. In Sample A, the growth temperature was dropped to $580\ ^\circ\text{C}$ after growth of the $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ layer in order to induce GPS immediately after the grade was restarted. In Sample B, H_2Se flow was turned on at the restart of the grade in order to induce GPS.

Figure 9 - EBIC Measurements of the isotype structures discussed in 3.4. Scale bar is 10 μm .

Table 1 – Dislocation glide distribution at different points in the grade and threading dislocation density for the samples discussed in Section 3.4.

	% of glide on B+ ($1\bar{1}1$) in first $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage	% of glide on B+ ($1\bar{1}1$) at the start of the second $\text{Ga}_x\text{In}_{1-x}\text{P}$ stage	Threading Dislocation Density (cm^{-2})
Control	98	79	$1.0\text{-}1.2 \times 10^7$
Sample A	95	46	$0.8\text{-}1.0 \times 10^7$
Sample B	96	33	$3\text{-}5 \times 10^6$