Defect Formation and Strain Relaxation in graded GaPAs/GaAs, GaNAs/GaAs and GaInNAs/Ge Buffer Systems for high-efficiency Solar Cells

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Abstract. Transmission electron microscopy of cross-section specimens and high-resolution X-ray diffraction analyses have been applied to investigate the formation of defects and the relaxation of layer strain in step-graded GaP\(_{x}\)As\(_{1-x}\) and GaN\(_{y}\)As\(_{1-y}\) buffer layer systems grown by metal-organic vapour phase epitaxy on GaAs (001) substrates with 6° miscut towards (111)A. The investigations have been complemented by characterization of the layer surfaces employing optical microscopy. The comparison of the different buffer concepts reveals characteristic differences in the formation of defects and in the relaxation of tensile layer strain. For GaPAs layers dislocations and microtwins form, releasing the major part of the tensile misfit strain. In contrast, for GaNAs dislocations and microtwins are largely absent, at least in the upper part of the buffer structure, and microcracks are generated. Consequently, during subsequent growth of layers with tensile strain, strain relaxation and defect formation can be effectively hindered by introducing intermediate GaN\(_{y}\)As\(_{1-y}\) layers with concentrations \(y > 2\%\) into a GaAs\(_{1-x}\)P\(_x\) buffer structure [1]. A similar concept can be used for layer systems with compressive strain, however, modified by using layers of differing alloy composition. The use of dilute nitride layers appears to offer a new concept for engineering defect distributions and layer strain in lattice-mismatched compound semiconductor layer structures. Such concepts are of particular interest not only but especially also for applications in high-efficiency III-V solar cells.

1. Introduction

For many technological components of the semiconductor industry, heteroepitaxial buffer layer systems with well engineered defect distributions and distributions of layer strain are essential for determining and optimizing device properties. Some examples are high-efficiency lattice-mismatched multi-junction solar cells based on III-V compound semiconductors [2], optoelectronic integrated circuits on Si [3], and vertical cavity surface emitting lasers [4].

The key issue in heteroepitaxial layer growth for device components is the control of the layer strains and of the type and distribution of potentially formed defects which may have detrimental effects on the electronic properties and on the long-term stability. For instance, the alloying of III-V compound semiconductors with defined concentrations of N allows engineering the band gap and lattice constant. The use of such dilute nitride compounds, like GaNAs and GaNP, for the epitaxial growth of buffer layers is particularly challenging under conditions of lattice-mismatch since these alloys show plastic properties which are drastically different from those of conventional ternary alloys, like GaPAs or GaInAs [5]. Already small concentrations of nitrogen may lead to considerable alloy hardening thus aggravating the formation and glide of dislocations [5-8]. High-quality strain-relaxed layers are difficult to obtain [7,8,10,11]. For these epitaxial layers, the strain relaxation is consequently not well described any more by equilibrium models, like the classical model by Matthews and Blakeslee [9].
While the effect of hardening of dilute nitride semiconductor compounds has mainly been recognized as a problem, we show in this paper that the phenomenon can actually be used as a concept for controlling defect formation and strain relaxation in lattice-mismatched hetero-epitaxy. From comparing defect formation and strain relaxation in step-graded GaP$_x$As$_{1-x}$ and GaN$_y$As$_{1-y}$ buffer layer systems composed of similar layer sequences, we observe that characteristic differences in the formation of defects and in the strain relaxation of layers with tensile strain occur. The use of layers of ternary compounds GaN$_y$As$_{1-y}$ with N-concentrations that exceed a threshold value $y$ of about 2% are effective in suppressing the formation of dislocations. Such layers are thus beneficial for layer epitaxy aiming at a control of layer strain and of defect distributions.

2. Experimental

Two step-graded buffer structures, GaP$_x$As$_{1-x}$ buffer layer system (buffer A) and GaN$_y$As$_{1-y}$ buffer layer system (buffer B), were grown by metal-organic vapour phase epitaxy (MOVPE) in an Aixtron AIX2600-G3 reactor on vicinal GaAs (001) substrates with 6° miscut towards (111)A [12]. Before buffer growth, a GaAs nucleation layer with a thickness of around 350 nm was deposited. Precursors for the phosphor layer growth were trimethylgallium (TMGa), arsine (AsH$_3$) and phosphine (PH$_3$). For the nitride buffer layer growth trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used. Figure 1 schematically gives the nominal data about the two systems. Both, the GaP$_x$As$_{1-x}$-system and the GaN$_y$As$_{1-y}$-system consist of eight layers for which the P- or N-content, respectively, is increased in fixed concentration steps for subsequent layers. In the following, we call these systems step-graded buffer layer systems. In order to improve strain relaxation, the layer system is capped with 2 layers, an individual layer whose P- or N-concentration, respectively, deviates from the grading sequence towards a higher concentration, and a layer repeating the P- or N-concentration, respectively, of the second last layer grown.

![Figure 1: Nominal buffer layer compositions x and y for the GaP$_x$As$_{1-x}$/GaAs buffer system A (left) and the GaN$_y$As$_{1-y}$/GaAs buffer system B (right).](image)

The respective growth temperatures, the reactor pressures and the V/III flux ratios were 580 °C, 70 mbar and ~ 17 for the GaP$_x$As$_{1-x}$ layers, and 573 °C, 70 mbar and ~ 3 for the GaN$_y$As$_{1-y}$ buffer layers. The gradings of the layer concentrations were chosen such that the two structures possess...
similar relative misfit profiles. The P- and N- concentrations in the topmost buffer layers correspond to a (negative) lattice misfit of ~ -1 % with respect to the substrate (estimated assuming Vegard’s law). The individual layers of the graded P- and N-containing structures possess nominal thicknesses of 170 nm and 200 nm, respectively. Only the topmost layers for buffers A and B are thicker, namely 420 nm and 500 nm.

A third set of compressive strained step-graded buffer structures was grown by MOVPE on a Ge-substrate with 6° miscut towards (111). The buffer contained GaIn$_{1-z}$As$_{z}$ layers with and without integrated GaInNAs intermediate layer. The individual layers had a nominal thickness of 200 nm. The GaInNAs intermediate layer was grown lattice matched onto the buffer layer. Trimethylindium (TMIn) was used as indium precursor.

The strain states of the individual layers of the buffer systems were determined from reciprocal space maps (RSM) measured by a Philips X’Pert PRO high-resolution X-ray diffractometry (XRD) system, i.e. by measuring the diffracted intensity distributions around the (004) reflections and around (2-24) and (224) reflections and to deduce the strain of individual layers from the corresponding lattice distances. The intensity distributions around (004) reflections are sensitive to layer strain whereas the intensity distributions around (2-24) and (224) reflections are sensitive to layer tilt. The (2-24) and (224) RSM measurements, respectively, were taken from the lattice planes parallel and perpendicular to the edges of the crystallographic steps induced by the substrate miscuts. In the following we use the terms “parallel to” or “perpendicular to step-edges”. A crystallographic layer tilt correction has been performed for the RS maps measured perpendicular to the “step edges” by applying the data from the symmetric (004) RSM.

The microstructure, the defects and interfaces were investigated in [110] and [1-10] lattice directions by methods of transmission electron microscopy (TEM) on cross-section samples. The TEM experiments were performed using a Philips CM30 electron microscope at 300 kV and, for high-resolution lattice imaging, a FEI TECNAI F30 at 300kV. Complementing information on the surface morphologies of the buffer layers were obtained from optical microscopy.

3. Results

3.1 Step-graded GaP$_{x}$As$_{1-x}$ buffer layer system (buffer A)

The residual strain of the individual buffer layers in the two in-plane <110>-directions is determined from symmetric (004) and asymmetric (2-24) and (224) RSM measurements, respectively. As example, Figure 2 displays the two asymmetric RS maps. From these RSM measurements we obtain quantitative values for the elastic strain of the individual layers. From these strain analyses it can be deduced that for the upper buffer layer, the strain levels in the direction parallel and perpendicular to the “step-edges” amount to about 30 % and 32 % of the total nominal misfit, respectively. From these values of the residual layer strain it can be concluded that buffer A is highly strain-relaxed.

TEM investigations of sample cross-sections indicate that misfit dislocations have been formed throughout the buffer layer system (Figure 3). The density of dislocations decreases towards the surface. Parallel to the “step-edges” (not shown here) occasionally cracks and microtwins are observed to form. It has been observed also before that the formation of microtwins, stacking faults and cracks is a common phenomenon in layer structures grown under conditions of negative misfit [13]. The role which these defects play for layer strain and for the surface morphology in our case will be discussed in Ch. 4.
Figure 2: Asymmetric (2-24) and (224) RSM of buffer A. The maps show the distribution of diffracted intensities in projections along [1-10] and [110]-direction. Qx and Qy are the reciprocal lattice units in directions parallel and perpendicular to the sample surface, respectively. The colour code depicts increasing intensities as spectral colours (from blue for low to red for high intensities). The crosses indicate the measured positions of the intensity maxima in reciprocal space for the different regions. The line drawn through the substrate peak depicts the expected distribution of intensity maxima from the layers within the buffer system for the case that the buffer layers show 100 % strain relaxation (analogous to a thick relaxed layer). Note that the buffer system reveals a high degree of strain relaxation in both in-plane <110>-directions as the map shows intensity concentrations close to the line of 100 % relaxation (see text).

Figure 3: TEM bright-field images of buffer A: overview of layer system imaged in the [1-10]-direction parallel to the “step-edges” (left) and in the [110]-direction perpendicular to the “step-edges” (right). The position of the interface is marked. Note the high density of dislocations. Only few cracks and a number of microtwins can be detected in the direction parallel to the “step-edges” (not visible in the picture shown above).
Analyses by light-optical microscopy allow for the inspection on a larger dimension scale. Figure 4 shows the presence of microcracks. The cracks are extending parallel to the “step-edges” in <1-10> substrate direction. The distances between the cracks range from about 500 µm to about 1000 µm.

**Figure 4:** Surface morphology of buffer A illustrated by means of a large-area overview in light-optical microscopy. The cross-hatch pattern parallel to the “step-edges” in [1-10]-direction is induced by dislocations and microtwins. Furthermore, cracks extending along <110> directions are visible.

### 3.2 Step-graded GaN$_x$As$_{1-y}$ buffer layer system (buffer B)

**Figure 5:** Asymmetric (2-24) and (224) RSM for buffer B. From these maps the relaxation of each individual buffer layer in both in-plane <110>-directions can be determined. In the direction parallel to the “step-edges” the upper buffer layer reveals a degree of strain relaxation of about 14 % and in the direction perpendicular to the “step-edges” of about 23 %, respectively. Note that the RSMs of the buffer system B shows a strong deviation from the intensity distributions expected to occur for complete relaxation of layer strains (see text).

As for the buffer A, the residual strain of the layers of buffer B in the two perpendicular in-plane <110>-directions can be determined from symmetric (004) and asymmetric (2-24) and (224) RSM measurements. Figure 5 shows as example two asymmetric (2-24) and (224) RSM measurements from buffer B. By means of these X-ray measurements the degree of strain relaxation of each individual buffer layer can be estimated as each layer contributes to the distribution of diffracted intensity[11].
Again, a tilt correction is necessary for the measurement in the direction perpendicular to the “step-edges”. By applying RSM measurements in the directions parallel and perpendicular to the substrate off-cut, we detect a slight asymmetry in the strain relaxation of buffer B. Next to the influence of the substrate off-cut on the symmetry, the asymmetry may emerge from the different behaviour of $\alpha$ and $\beta$ dislocations in diluted nitrides. The broadening of the substrate intensity peak can be attributed to a lattice bending which results from the coating with an epitaxial buffer layer system with layer mismatch. From these RSM measurements we gain an overview about the strain state of the buffer layer system and can obtain quantitative values for the elastic strain of the individual layers of the buffer B. Qualitatively, the measurements reveal that the strain in the lower three GaN$_x$As$_{1-x}$-layers is almost completely relaxed whereas almost no strain relaxation has occurred in the upper layers. The measurements reveal a strain relaxation of more than 70 % for the first two buffer layers in both in-plane $<$110$>$-directions. For the subsequent buffer layers, the degree of strain relaxation decreases rapidly. The uppermost buffer layer finally shows a degree of strain relaxation of around 14 % in the direction parallel to the “step-edges” and of around 23 % in the direction perpendicular to the “step-edges”, respectively. These observations indicate that significant differences exist in the strain relaxation behaviour for the lower and the upper buffer layers. This behaviour is clearly different from the experimental results obtained for buffer A.

![Figure 6](image-url) Cross-section TEM dark-field images of buffer B in [1-10]-direction parallel to the “step-edges” (left) and in [110]-direction perpendicular to the “step-edges” (right): overview of layer system with regions showing dislocations and microcracks. The presence of dislocations is observed for layers with a “threshold” concentration of N of around 2 %. Beyond this value, no dislocations are observed. Instead, microcracks are observed whose formation can be attributed to cumulative tensile layer strain. In [1-10]-direction, dislocations are observed which also extend into the GaAs substrate.

The TEM investigations of cross-section samples of buffer B show that essentially dislocations and microcracks have formed parallel to the “step-edges” as well as perpendicular to the “step-edges”. Figure 6 shows as example that the dislocations are present only in the layers of the lower part of the buffer, with nominal N concentrations $y < 2 \%$ (cf. Figure 1). When imaging parallel to the “step-edges”, a considerable number of dislocations can be observed in the GaAs substrate. In contrast, no dislocations are formed in the upper part of the buffer system where the layers have a nominal N concentration $y > 2 \%$. Instead, in the two mutually perpendicular $<$110$>$-directions, microcracks and occasionally also microtwins (not shown here) are formed.
Figure 7: Optical micrograph of surface area of buffer B showing microcracks (dark contrast lines) extending along both <110>-directions.

Observations by light-optical microscopy show that microcracks have formed and propagated along both <110> substrate directions (Figure 7). The distances between the cracks are in the range of 50 µm to 500 µm. Some of the cracks are blocking each other.

3.3 Step-graded Ga$_{1-x}$In$_x$As buffers with integrated nitride blocking layer

Figure 8: TEM bright-field micrographs of Ga$_{1-x}$In$_x$As/Ge step-graded buffer structures without (left) and with (right) GaInNAs intermediate layer deposited onto a step-graded buffer system and capped by a GaInAs top buffer layer. Formation of dislocations in the top buffer layer is not observed (right).

Figure 8 shows a section of the dislocation network of a Ga$_{1-x}$In$_x$As buffer system without (left) and with an integrated GaInNAs intermediate layer (right). In the first case, dislocations are present also in the upper part of the structure. In contrast, dislocations are absent and obviously hindered from gliding into the topmost buffer layer during layer growth when a GaInNAs intermediate layer is introduced.
Figure 9 shows the angular dependence of the diffracted X-ray intensity for the GaInAs buffer region, the Ge layer, and the top buffer region as revealed by high resolution X-ray rocking curves measured for the two cases. The comparison reveals that the full width at half maximum (FWHM) value of the intensity peak generated by the top buffer layer is reduced by about 15 % for the case of the buffer containing a GaInNAs layer. This decrease of the FWHM value can be interpreted as signature of a low density of dislocations within the upper buffer layer since the presence of significant numbers of threading dislocations would cause measurable broadening of the intensity peaks in rocking curve measurements.

![Graph showing X-ray diffraction data for GaInAs buffer and GaInNAs buffer with GaInNAs-layer](image)

**Figure 9**: High resolution X-ray diffraction measurement of the two Ga$_{1-x}$In$_x$As/Ge step-graded buffer structures (cf. Figure 8). The decrease in the full width at half maximum (FWHM) of the intensity peak originating from the diffraction of the top buffer layers is consistent with the TEM observation of a strongly reduced dislocation density originating from the application of a nitride layer.

4. Discussion

Characteristic for the step-graded GaPAs buffer system is the strain relaxation via formation of misfit dislocations and microtwins (Figure 3). The residual strain stays low enough to avoid crack propagation. In contrast, the formation of misfit dislocations during the growth of the first layers and the subsequent formation of microcracks during further buffer growth is characteristic for the GaNAs buffer system (Figure 6). Obviously, the suppression of dislocation formation in the upper part of the structure leads to an increase of the residual strain (due to the lattice grading) so that the system reaches strain values for which crack formation and propagation becomes possible.

4.1 Development of the buffer microstructures during layer growth

The microstructure observations (Ch.3) reveal significant differences in the strain relaxation behaviour of the investigated buffer systems. The two buffer layer systems which were designed for this investigation represent cases for which the strains of the individual layers are tensile in nature. This situation is achieved in a controlled way by adding P or N to crystalline GaAs and reduces the lattice constants of the resulting alloy to a lesser (by adding P) or a higher degree (by adding N).
For the first case of a step-graded GaP<sub>x</sub>As<sub>1-x</sub> system (buffer A, Ch. 3.1), we observe that the microstructure develops predominantly by forming misfit dislocations and microtwins. Crystalline defects like dislocations, stacking faults, and twins are known to be effective in releasing misfit strain during the epitaxial growth of layers [14]. In our case, the observation of such defects is regarded as being the direct result of the relaxation of layer strain. From the RSM measurements (Figure 2) it is deduced as well that the buffer A is highly strain-relaxed, with a remaining residual strain of about 30% of the original strain in the upper layers in the both mutually perpendicular <110>-directions. Only few microcracks are detected in such buffer systems proceeding in the direction parallel to the “step-edges”. This clearly indicates that the major part of the stress for this buffer is relieved effectively by forming dislocations and microtwins.

In contrast, for the step-graded GaN<sub>y</sub>As<sub>1-y</sub> buffer layer system (buffer B, Ch. 3.2) misfit dislocations form only within the first three layers of low N content. The composition grading of this layer system corresponds to a relative increase in lattice misfit by up to about 0.3%. The RSM measurements (Figure 5) reveal indeed a large degree of strain relaxation of around 70% and 85% of the original values for the first and second buffer layer, respectively. Misfit dislocations are absent for the upper layers of the buffer system containing N contents <i>y</i> &gt; 2%. Instead, microcracks extending along the two mutually perpendicular <110> directions form in high numbers in these buffer regions (Figures 6, 7). The corresponding RSM measurements (Figure 5) show that these layers are still kept under large tensile layer strain whose magnitude increases stepwise with the distance from the substrate, corresponding to the increase of the lattice-misfit by up to 1%. Compared with a fully strained layer, i.e., assuming a strain value based on a calculated lattice misfit related to the layer composition, the residual strain in the upper layers is still of the order of 80%. These results indicate that the observed microcracks do not significantly contribute to the relaxation of strain, and that only part of the misfit strain is relaxed by forming cracks. Dislocation formation and movement of dislocations are largely suppressed in this part of the buffer system.

Adding small amounts of nitrogen to GaAs has effects on the electronic properties and on the mechanical properties. On the one hand, the band-gap energy of GaN<sub>y</sub>As<sub>1-y</sub> decreases, and on the other hand the material becomes harder which may result in a reduced dislocation mobility [5]. The TEM results (Figure 6) and the X-ray measurements (Figure 5) convincingly demonstrate that diluted GaN<sub>y</sub>As<sub>1-y</sub> layers with <i>y</i> &gt; 2% are effective in hindering misfit dislocations from threading through the bulk material of mismatched semiconductor heterostructures. Hence, strain relaxation is aggravated for the subsequently grown layers. This effect can be attributed to the effect of the substitutional nitrogen atoms which, due to their small covalent radius, lead to local lattice perturbations that decrease the dislocation mobility [5]. Furthermore, alloy hardening may induce a pinning of dislocations which will lead to further contributions to strain hardening.

As can be concluded from the TEM results (Figure 6, Ch. 3.2) and from the RSM measurements (Figure 5, Ch. 3.2), this characteristic behaviour is not observed when the nitrogen concentration is below a threshold value of around 2%. By applying RSM measurements in the directions parallel and perpendicular to the substrate off-cut, we have detected a slight asymmetry in the strain relaxation of buffer B. Next to the influence of the substrate off-cut on the symmetry, the asymmetry may emerge from the different behaviour of α and β dislocations in diluted nitrides.

Comparing the two buffers A and B, we arrive at the conclusion that for the GaP<sub>x</sub>As<sub>1-x</sub> buffer the behaviour is nearly reversed. As the material becomes softer by adding phosphorous the dislocations feel a weaker Peierls potential in the upper GaP<sub>x</sub>As<sub>1-x</sub> buffer layers. This favours dislocation glide and propagation and thus leads to the generation of a very high dislocation density by means of dislocation multiplication.

4.2 Comparison with critical layer thickness for defect formation in single layers

We discuss the observations for buffer systems A and B in regard with simple estimates for a critical layer thickness for defect formation under conditions of negative misfit.
For layer systems with low mismatch, theoretical considerations which are based on the equilibrium theory of Matthews and Blakeslee [9] allow to estimate a critical layer thickness for defect formation and a critical thickness for the fracture of strained brittle materials [15]. The thickness beyond which a single pseudomorphic layer grown epitaxially on a substrate starts to release strain by the formation of misfit dislocations is given by

\[ h_{c,\text{dislocation}} = \frac{b}{8\pi f \cdot (1 + \nu)} \left( \ln \frac{h}{b} + 1 \right) \]  

with \( b \) the length of the Burgers vector (assuming the formation of perfect 60° misfit dislocations), \( h \) the layer thickness, \( f \) the lattice-misfit between layer and substrate and \( \nu \) the Poisson ratio.

For systems with higher lattice mismatch the critical thickness for the formation of cracks is given by

\[ h_{c,\text{crack}} = \frac{a \cdot (1 - \nu)^2}{5\pi f^2} \]  

with \( a \) the lattice constant of the respective materials, \( f \) the lattice misfit, and \( \nu \) the Poisson ratio. The critical misfit for spontaneous fracture is described by

\[ f_{c,\text{fracture}} = \frac{(1 - \nu)}{10}. \]  

For the cases of a GaPAs layer and a GaNAs layer on a GaAs substrate, respectively, Figure 10 (A) shows the result of the calculated critical thickness for different values of misfit \( f \) according to equation (1), assuming a value \( \nu = 0.32 \) for GaPAs and GaNAs. Figure 10 (B) shows the calculated values (equ. 2) for the critical thickness for cracking for a GaPAs layer and for a GaNAs layer on a GaAs substrate as function of the misfit \( f \), assuming the same values for \( \nu \). Figure 10 (C) represents the situation for the critical strain for spontaneous fracture calculated to occur at a misfit value of 7 % according to equ. 3. Such values for the misfit of layers on GaAs substrates can indeed be theoretically achieved for GaNAs layers with sufficiently high N contents but cannot be achieved for GaPAs layers for which the maximum lattice misfit that can be realized will be about 3.6 %. Therefore, spontaneous fracture of GaPAs layers is not expected to occur.

Figure 10 also qualitatively illustrates the different strain relaxation behaviour of the two buffer systems A and B (arrows) observed in our experiments. For buffer A, the average lattice misfit is \( f_{\text{GaPAs,av}} \approx -0.65 \% \). Therefore, the theoretical values for the critical thickness for dislocation and crack formation in GaPAs (with \( f = -0.65 \% \) lattice-misfit to the substrate) are about 5 nm and 400 nm, respectively. Continuous strain relaxation by formation of misfit dislocations and microtwins as observed for this buffer system (Figure 3) therefore leads to the situation that the residual strain stays low enough during layer growth to avoid crack propagation. Starting with a completely strained state (at a layer misfit of around 0.1 %), this development is schematically illustrated by the blue arrow.
Figure 10: Residual strain, expressed by the misfit $f$ of an individual layer, versus film thickness. Theoretical critical layer thickness for dislocation formation (line A), crack formation (line B) and spontaneous film fracture (line C). Illustrated by arrows are the regions of different microstructure development during layer growth based on the predictions for single layer growth. The observed strain relaxation paths during layer growth for the buffer layer systems A and B are schematically illustrated by the coloured arrows (see text for details).

For buffer B, the estimated value for the average lattice misfit amounts to about -0.5 %. The theoretical estimates for the critical thickness for dislocation and crack formation result in 6 nm and 650 nm, respectively. During growth of the step-graded GaNAs buffer system, the misfit strain starts to relax already during the growth of the first layer by the formation of misfit dislocations (Fig. 6). We could observe that this mode of strain relaxation stops after the deposition of the third layer. Above a layer thickness of around 700 nm, microcracks form that contribute only little to releasing the misfit strain. This suppression of dislocation formation in the upper part of the structure leads to a situation where during further layer growth the residual strain due to the lattice grading increases until finally cracks form and propagate. This development is schematically illustrated by the red arrow. While the overall strain relaxation behaviour can be interpreted qualitatively in this way, a more quantitative analysis would need to consider the grading of layer composition.

4.3 Role of alloying additions: P-based versus N-based buffer systems

The observed differences in microstructure development are likely to originate from the differences in microhardness of the ternary alloy layer materials and the resulting consequences for dislocation formation and dislocation mobility. For the dislocation movement, hard materials possessing high interatomic binding energies have a high Peierls potential. Microhardness values of binary compounds published in the literature yields ranges from 5 GPa to 7 GPa for GaAs [16], from 4 GPa to 6 GPa for GaP [17], and from 10 GPa to 20 GPa for GaN [16,18,19]. Based on these values it can be concluded that, by adding more and more P to the GaAs compound, the resulting ternary GaPAs compound semiconductor will tend to decrease the hardness and become softer. In contrast, by adding more and more N to GaAs, the ternary GaNAs compound semiconductor should increase its hardness.
Based on these considerations we conclude that dislocation gliding, propagation and multiplication is suppressed in the upper harder buffer layers of higher N content, or, in other words, dislocations are blocked from propagating into the upper layers for the GaNAs buffer layer system. As confirmed by our TEM investigations (Figure 6), these phenomena can still occur in the lower buffer layers which are ‘softer’ due to their low N content. The observation that dislocations are formed (‘reflected’) even in the GaAs substrate (Figure 6) confirms this point of view. The suppression of dislocation formation and propagation in the upper buffer layers is accompanied by the generation of high tensile strain leading to the observed crack formation. On the other hand, the continuous formation of dislocation arrangements and the gliding of dislocations during layer growth is very effective for the step-graded GaPAs buffer system, resulting in the gradient of dislocation density observed by TEM (Figure 3).

4.4 Strain engineering for high-efficiency solar cells: buffer systems of tensile and compressive strain

Both the GaPAs and the GaNAs buffer systems are multilayer systems under tensile strain. As we have discussed above for the GaNAs buffer layer system, dislocation gliding, propagation and multiplication is suppressed in the upper harder buffer layers of higher N content, and dislocations and microtwins are largely absent. Instead, microcracks form during the growth of the upper layers of the step-graded buffer system. Consequently, we can conclude from these studies that, during subsequent growth of layers with tensile strain, the strain relaxation by defect formation can be effectively hindered when introducing intermediate GaN\textsubscript{y}As\textsubscript{1-y} layers with adequately tailored N-concentrations \(y > 2\%)\) into a buffer structure. This concept has also been tested and has proven to be successful in a related study of GaP\textsubscript{x}As\textsubscript{1-x} buffer structures with an incorporated GaN\textsubscript{y}As\textsubscript{1-y} layer (for values of \(y\) ranging from \(-2.5\%)\) to \(-4\%)\) [1]. We conclude that the use of dilute nitride layers offers the possibility for new concepts for engineering defect distributions and layer strain in lattice-mismatched compound semiconductor layer structures. They are therefore of particular interest especially also for applications in high-efficiency III-V solar cells.

It could be shown by our study that a similar growth concept, modified by adding In to GaNAs, can be used as dislocation blocking layer for Ga\textsubscript{1-x}In\textsubscript{x}As/Ge buffer layer systems under compressive strain. This concept is similarly effective in controlling the defect formation and desired defect reduction in compressively strained heterostructures, making it a promising tool for growth of metamorphic high efficiency III-V multi-junction solar cells on GaAs, Ge or Si substrates.

5. Conclusions

Metamorphic step-graded GaP\textsubscript{x}As\textsubscript{1-x} and GaN\textsubscript{y}As\textsubscript{1-y} buffer layer systems were grown by metal-organic vapour phase epitaxy (MOVPE) on GaAs (001) substrates with a 6° miscut towards (111)A. Defect formation and strain relaxation have been investigated by transmission electron microscopy and high-resolution X-ray diffraction and were complemented by surface characterization employing optical microscopy.

The comparison of these different buffer systems under tensile strain revealed characteristic differences in the formation of defects and in the strain relaxation behaviour:

- The step-graded GaP\textsubscript{x}As\textsubscript{1-x} buffer layer system (buffer A) shows effective strain relaxation induced by the formation of dislocations and microtwins. HRXRD analyses reveal relatively small amounts of residual strain.

- The step-graded GaN\textsubscript{y}As\textsubscript{1-y} buffer layer system (buffer B) in contrast shows only low dislocation generation in the lower part but crack generation induced by cumulative tensile strain in the upper part of the buffer. Thus dislocation formation is suppressed by means of N-induced material hardening for an N-concentration higher than around 2\%.

12
Comparative investigations of a step-graded Ga$_{1-x}$In$_x$As buffer layer with integrated nitride blocking layer reveal a lower dislocation density in the upper buffer layer. Such nitride blocking layers therefore appear promising for defect engineering of metamorphic multi-junction solar cells.

Our observations indicate that for the GaPAs-system the relaxation of tensile strain is achieved by forming a high number of dislocations and microtwins. In contrast, for the GaNAs-system the tensile strain induces microcrack formation and only few dislocations and microtwins are generated. The differences in strain relaxation behaviour appear to reflect the differences in microhardness (or the Peierls potential) of the ternary alloy materials.

The usage of dilute nitride layers in buffer systems offers a new concept for engineering defect distributions and layer strain in lattice-mismatched compound semiconductor layer structures and is of particular interest especially also for applications in high-efficiency solar cells. Obviously, strain relaxation and formation of defects, such as misfit dislocations, can be effectively hindered during subsequent growth of layers when introducing intermediate GaN$_y$As$_{1-y}$ layers with concentrations $y > 2\%$. For layers under tensile strain, the concept has been tested and has proven to be successful also in a related study of GaP$_x$As$_{1-x}$ buffer structures with incorporated GaN$_y$As$_{1-y}$ layers (values of $y$ ranging from $-2.5\%$ to $-4\%$) [1]. On the other hand, the investigations presented in this paper show that successful defect engineering becomes possible as well for layer systems under compressive strain when using layers of differing alloy composition, for instance alloys containing In.

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