Effect of Sb-surfactant on GaInP CuPt_B type ordering: assessment through dark field TEM and aberration corrected - HAADF

C. Coll^a, E. Barrigón^a, L. López-Conesa^a, J. Rebled^a, L. Barrutia^b, I. Rey-Stolle^b, S. Estradé^a, C. Algora^b and F. Peiró^a

We report on the effect of Sb on the microstructure of GaInP layers grown by metal organic vapor phase epitaxy (MOVPE). These layers exhibit the CuPt_B single variant ordering due to the intentional misorientation of the substrate (Ge(001) substrates with 6° misorientation towards the nearest [111]). The use of Sb as surfactant during the GaInP growth does not modify the type of ordering, but it is found that order parameter (η) decreases with increasing Sb flux. Dark field microscopy reveals a variation of the angle of the antiphase boundaries (APB) with Sb amount. The microstructure is assessed through high angle annular dark field (HAADF) experiments and image simulation revealing Z-contrast loss in APB boundaries due to the superposition of ordered domains.

1 Introduction

GaInP is an important material in III-V optoelectronics and microelectronics, and is used today in a variety of semiconductor devices, namely, HBTs, HEMTs, LEDs, lasers and solar cells. In the particular field of multijunction solar cells (MJSC), GaInP is the material of choice for the top subcell in a variety of designs (i.e. lattice matched triple-junction GaInP/Ga(In)As/Ge, inverted metamorphic, upright metamorphic, wafer bonded and lattice-matched using dilute-nitride solar cells). Therefore, a deep understanding of the interplay between growth conditions and material microstructure is fundamental to further improve the performance of the aforementioned devices.

As many other III-V ternaries, GaInP presents a CuPt ordering in the group III sublattice. This ordering consists of alternating Ga- and In-rich {111} planes (i.e., $\text{Ga}_{0.5(1-\eta)}\text{In}_{0.5(1+\eta)}\text{P}$ / $\text{Ga}_{0.5(1+\eta)}\text{In}_{0.5(1-\eta)}\text{P}$), where η is defined as the order parameter. For a fully disordered GaInP material $\eta = 0$, whereas for a completely ordered material $\eta = 1$. Despite there being four equivalent {111} planes in the zinc-blende structure, ordering in GaInP grown on (001)-oriented substrates is only observed on the ($\bar{1}11$) and ($1\bar{1}1$) planes (i.e., CuPt_B structure with two variants) as evidenced by a double periodicity in electron diffraction patterns obtained in [110] cross-section views^{1,2}. Besides, misorientation of the (001) substrate by a few degrees towards (111) favors the formation of a single variant only³.

A careful control of the ordering in GaInP enables engineering of device properties since, among others, the degree of order modulates the energy bandgap (E_g) of the alloy, leading to a reduction in E_g of 100 meV in a totally ordered layer (the higher η , the lower E_g). Surfactants emerge as an alternative to control the degree of order without changing other growth parameters^{4,5}. Several species have been studied for this purpose in GaInP (e.g., Te, Sb, Bi and As), being Sb particularly effective to modulate the order parameter⁵⁻⁷.

Not only the degree of order of the alloy must be controlled but also its domain microstructure. Several studies have shown that the microstructure of ordered GaInP consists of domains of ordered material with a uniform phase separated by antiphase boundaries (APBs)⁸⁻¹¹. The shape and size of the domains strongly depend on the substrate misorientation¹² and growth conditions such as growth temperature¹³, growth rate¹² or V/III ratio¹⁴. The APBs typically form a characteristic angle θ_{APB} (measured from (001) towards the corresponding ordering plane), which has been reported so far to be determined only by substrate misorientation¹². The APB angle in single-variant ordered GaInP layers ranges approximately from 40° to 85° for GaAs wafers with miscut angles of 3° to 9°, respectively¹². APBs are of considerable importance, since they contribute to electron scattering and form defect levels¹⁵. Besides, the electrical and optical properties of GaInP are influenced by the ordered domains. On the one hand, the domain size affects the high-energy excitonic peak in low temperature photoluminescence (PL) measurements^{13,16}. On the other hand, the presence of ordered domains leads to anisotropy in the minority carrier diffusion length as well as in the layer conductivity¹⁷ and reduces carrier mobility¹⁸. In spite of the importance of Sb as a surfactant to modulate the order parameter during the growth of GaInP layers, there is no study on the microstructure of partially ordered GaInP alloys when employing Sb as a surfactant thus far in the literature. Moreover, despite electron diffraction and dark field (DF) imaging in conventional microscopy have been extensively used to analyse GaInP ordering, works revisiting III-V compounds ordering within the dimension of aberration corrected atomic resolution scanning transmission electron microscopy (STEM) are very scarce¹⁹. Accordingly, in the present work we undertake a systematic assessment of the impact of Sb on both the degree of ordering and the microstructure of GaInP layers, including the dependence of the θ_{APB} angle on the Sb/P ratio. In addition, the microstructure of the domains and their boundaries is elucidated using high angle annular dark field (STEM-HAADF) imaging and simulations.

^a LENS-MIND, Departamento de Electrónica, Instituto de Nanociencia y Nanotecnología (In2UB), Universidad de Barcelona, c/Martí Franqués 1, 08018, Barcelona, Spain

^b Instituto de Energía Solar, Universidad Politécnica de Madrid, Avda. Complutense 30, 28040 Madrid, Spain

Semiconductor structure	Sb/P (ppm)	η
A	0	0.53
B	411	0.48
C	728	0.43
D	1720	0.29

Table 1 Summary of the samples analyzed in this study. For details on η determination see Ref.²¹ $\eta = 1$ means a completely ordered GaInP material while $\eta=0$ means a disordered GaInP material.

2 Experimental details

Semiconductor structures were grown in a horizontal MOVPE reactor (Aixtron AIX200/4) equipped with an in situ reflectance anisotropy (RA) spectrometer (LayTec EpiRAS 200). Since our main focus regarding the use of GaInP layers is on multijunction solar cells, we used Ge(001) substrates with 6° misorientation towards the nearest [110]. The Sb precursor employed was TESb. The epitaxial structures can be seen in Fig.1(a). They all consist of a 365 nm thick GaInP nucleation layer (details on the growth of the GaInP nucleation on Ge can be found in²⁰) followed by a Zn-doped, 1100 nm thick GaInP layer, where different amounts of Sb were introduced in the reactor to promote surfactant mediated growth. Hereafter, this layer will be called the layer of interest (LOI). The growth conditions of the GaInP LOI (growth temperature of 675°C , V/III ratio of 120, growth rate of 0.60 nm/s) are commonly employed for the growth of the top cell base of lattice-matched triple-junction solar cells²⁰. The effect of Sb is very sensitive to growth conditions and reactor geometry –the surfactant action of Sb is determined by the amount of Sb that eventually reaches the growth surface– and thus we have developed a method to calibrate the injected molar flow of Sb to obtain the desired order parameter²¹. Throughout the rest of the text, the molar flow is going to be expressed in terms of the Sb/P ratio in the gas phase, in parts per million. A summary of the samples analyzed with the employed Sb/P ratios can be seen in Table 1, together with their η (order parameter) value as determined in²¹, from PL and X-Ray Diffraction (XRD). In order to guarantee a steady state Sb coverage of the surface, after the completion of the GaInP nucleation layer the growth was interrupted, then the Sb flow was switched on for 20 seconds, and subsequently the growth of the GaInP:Sb buffer layer proceeded keeping the Sb flow unchanged²¹. For TEM characterization, structures were thinned up to electron transparency using a Focused Ion Beam (FIB) lift out procedure. Samples were prepared in the two orthogonal [110] and $[1\bar{1}0]$ directions in order to unambiguously investigate the type of CuPt ordering existing in the layers. Conventional DF and selected area electron diffraction (SAED) observations were carried out in a JEOL 2100 operated at 200kV. An aberration corrected Titan FEI instrument operated at 300kV was used for high resolution high angle annular dark field imaging (HAADF) in scanning transmission (STEM) mode.

3 Results and discussion

Conventional low magnification bright field TEM images, as the one shown in Fig.1(a) as an example, confirm the high quality of all samples. No trace of anti-phase domains —due to coalescence of zinc-blende phases typically encountered in III-V materials grown on group IV substrates²— was observed for any sample at the GaInP/Ge heterointerface (see Fig.1(b)). Therefore, we can discard any influence of the III-V/IV heteroepitaxy in the microstructure of the upper layers grown using Sb. In addition, no evidence of GaInP decomposition was found in any of the examined samples. This was avoided by the use of relatively low Sb/P ratios and high growth rates²².

The relative positions of the group III and group V atoms in the dumbbells of $\langle 110 \rangle$ cross-sections of the structures were determined through Z-contrast STEM-HAADF images. Fig.1(c) and (d) present the projection of the dumbbells of GaInP viewed along the [110] and $[1\bar{1}0]$ zone axes, respectively. The group V element (light element, lower intensity) is over (below) the element of group III (heavier atom, higher intensity) in $[110]$ ($[1\bar{1}0]$) view, as expected from³.

Accordingly, Fig.2 shows the selected area electron diffraction patterns (SAED) of the LOI in the structures in cross-section geometry along the [110] and $[1\bar{1}0]$ directions for the different Sb/P ratios employed. As it can be observed, all samples observed in $[1\bar{1}0]$ zone axis show the expected pure zinc-blende pattern. On the contrary, SAED patterns of all the [110] oriented samples include extra satellite spots at positions $(h \pm 1/2, k \mp 1/2, l \pm 1/2)$. These results show the existence of a CuPt_B ordering in the $(1\bar{1}1)$ plane with only one variant for all samples, which indicates that Sb does not change the type of ordering (CuPt_A vs CuPt_B, or single vs double variant) that would be expected for GaInP grown on a highly misoriented substrate³. The variations on the degree of order amongst the different samples can be qualitatively inferred by comparing the ratio of intensities between the $1/2\{111\}$ superlattice spots and the usual zinc-blend spots in the same diffraction pattern. As the Sb/P ratio is increased, the relative intensity of the $1/2\{111\}$ spot becomes weaker, which indicates that Sb is actually decreasing the order parameter (Fig.2). This is in good agreement with the decrease in η with Sb/P ratio as summarized in Table 1.

On the other hand, Fig.3 shows dark field electron microscope images obtained using the satellite spot $(1/2, 1/2, 1/2)$. All samples are seen to present a single-variant domain structure separated by APB dark stripes. In the sample grown as a benchmark (i.e., Sb/P = 0 ppm), the APBs originate from the heterointerface GaInP/Ge with a θ_{APB} lower than the value previously reported for GaInP grown on GaAs with the same offset (aprox. 65°)¹². In this case where no Sb is used, the nucleation layer cannot be distinguished from the buffer layer according to the microstructure (i.e. the orientation of the APBs is the same in both the GaInP/Ge nucleation layer and the

Fig. 1 (a) General low magnification view in bright field mode of the semiconductor structures analyzed in this work. (b) HAADF image of the interface between the GaInP nucleation layer and the Ge substrate. (c) and (d) Filtered high resolution Z-contrast HAADF image of the dumbbells of GaInP:Sb viewed along the $[110]$ (c) and $[1\bar{1}0]$ (d) zone axes. The group V element is over (below) the group III element in $[110]$ ($[1\bar{1}0]$) view.

LOI). On the contrary, θ_{APB} is significantly modified in GaInP once Sb is employed during growth and, therefore, a clear change in θ_{APB} is observable between the nucleation layer and the LOI (see Figs.3(b) and 3(c)). However, since unavoidable strain contrast and bend contours are present at the GaInP (nucleation)/GaInP:Sb(LOI) interface in these dark field imaging mode images, it is not possible to distinguish whether the APBs propagate from the nucleation to the LOI layers or new APBs are created just at the interface between them. Fig.3(d) shows the evolution of the average value of θ_{APB} versus the Sb/P ratio employed for the growth of the LOI. The θ_{APB} monotonically increases with the Sb/P ratio, reaching values higher than 90° for Sb/P ratios of 728 ppm. As far as we know, such high θ_{APB} values have only been observed in other materials such as in GaInAs layers grown on InP substrates²³. It should be noted that the quantitative relationship between θ_{APB} and Sb/P gaseous molar flow ratio found in this work has only an exemplary content since it depends on both reactor configuration and geometry. Yet, the trend is relevant.

The extension angle of the APBs has been directly correlated to the use of Sb –which is known to change the surface reconstruction of the GaInP– yielding θ_{APB} values even higher than 90° . As explained in²⁴, APBs are active sites for nucleation of 2D islands on the terrace of vicinal surfaces. The growth and collision of these 2D islands with a normal step extend the APB in a particular direction²³. So far, it has been reported that θ_{APB} only changes significantly with wafer offcut¹². Here, we report that the extension angle of the APB is also affected by the different amount of Sb introduced during the growth of the semiconductor structures. Since Sb modulates the order degree through changes in the surface reconstruction²⁵, we tentatively link the microstructure formation (i.e., θ_{APB}) with the surface reconstruction. Since we are using high offcut substrates (6° misorientation towards the nearest $[111]$), step reconstruction variation due to Sb should also be considered.

More quantitative measurements concerning the domain size were also carried out to relate them with η . The average domain width (measured as the average horizontal extension of a domain limited by the dark stripes of the APBs) as a function of the distance to the substrate was chosen as a control parameter. At this point it is worth noting that in the past two competing interpretations have been published to explain DF images of partially ordered GaInP as the ones shown in figure 3. In the early days, some authors reported the dark areas to be perfectly disordered regions whilst bright areas corresponded to ordered domains, being the order parameter given the balance between these two areas. This explanation was superseded by the now widely accepted vision that interprets the bright regions as domains of a given η parameter being the dark regions their boundaries where antiphase domains meet and overlap as is suggested in¹⁰. Our quantitative analyses on the images of figure 3, add evidence to the latter explanation. For instance, no clear dependency was found between Sb flux and domain size. In other words, the average width of bright contrast regions in Fig. 3 (i.e. DF images obtained

Fig. 2 Comparison of the selected area diffraction patterns of the LOI in the structures along the $[110]$ zone axis (top panels) and $[1\bar{1}0]$ zone axis (bottom panels) as a function of the employed Sb/P ratio. Notice the superstructure reflections between the main spots in the direction parallel to $g=(111)$ in the $[011]$ zone axis diffraction patterns only. The yellow arrow indicates the $[001]$ direction in all cases.

selecting the satellite spot) does not show a correlation with Sb flux whereas the order parameter does. This fact is incompatible with the dark regions being fully disordered GaInP since, if these were the case, they should increase in area as the order parameter decreases. Therefore, in order to clarify the precise nature of these dark areas, an aberration corrected HAADF characterization was carried out. In Fig.4(a) we can clearly see the CuPt_B single variant ordering on $[1\bar{1}1]$ through alternation of In-rich (higher-Z, bright) and Ga-rich (lower-Z, dark) planes.

This double periodicity of the microstructure is evidenced by the presence of the superstructure spot in the fast fourier transform (FFT) of the HAADF image (Fig.4(b)). Moreover, the specific shape of the domain boundaries was analyzed by applying a mask on the FFTs, selecting the satellite spot only, as shown in Fig.4(c). This allows obtaining an inverse FFT image, where ordered regions are highlighted, thus getting the domain boundaries in sharp relief. Apparently, the FFT image corresponds to the contrast observed at lower magnification in the DF image in figure 3(a), in terms of APB angle, and ordered/disordered appearance. Notice, in figure 4(a), the loss of Z-contrast right in the APB detected in the filtered image (Fig.4(c)), that could be attributed to a disordered region. As the electrical properties depend on the degree of order in the LOI and the orientation of the domains it is imperative to clarify the microstructure of the film (i.e. nature of the bright and dark regions in Figure 3). In this way, a correct correlation can be established between the structural characterization and the electrical performance.

Accordingly, to get a deeper understanding of the images presented, we performed HAADF-STEM simulations. The TEMsim package², which calculate high resolution conventional and scanning transmission electron microscope images of thin specimens from first principles using the multislice method for electrons, was used to that purpose. We propose an atomistic model consisting on a superposition of two blocks of GaInP oriented in $[110]$ zone axis with a displacement of half a unit cell in the perpendicular direction between them. The total thickness of the block is $h = 60\text{\AA}$ and has been kept constant. A scheme of this atomistic model is shown in Fig.5(a), where the darkest region (which thickness is given as a fraction of h) corresponds to the displaced block. Several simulations were performed for different thicknesses (t). From the simulated images, we measured the intensity profiles perpendicularly to the ordered planes, which are along the $[1\bar{1}1]$ direction. The results are presented in figure 5(c); for values above $t = 0.35h$ the Z-contrast due to ordering is still visible. Nevertheless, for thickness values equal and below $t = 0.3h$ the intensity variation flattens out. The simulated HAADF-STEM images (Fig.5(b)) show that the order of (111) In rich/Ga rich planes is easily seen for thick superposed layers and that, as the superposed layer gets thinner, the ordering becomes indistinguishable. A thin enough ordered region displaced with respect to another underneath ordered region does effectively appear as the characteristic Z-contrast of a sample without order. Therefore, in the light of this simulations, the presence of dark areas in the DF images can be totally accounted for as the superposition of antiphase domains.

Fig. 3 Dark field TEM images obtained along the $[110]$ zone axes using the satellite spot $g=(1/2, -1/2, 1/2)$ (a) with no Sb; (b) with a Sb/P ratio of 411 ppm; (c) with a Sb/P ratio of 728 ppm. (d) Schematic representation of the change in orientation of ordered domains (angle θ_{APB} as a function of Sb/P ratio).

Fig. 4 (a) HAADF-STEM image of sample B a long $[110]$ zone axis. (b) FFT of the whole area and, highlighted in green, applied mask selecting the satellite spots. (c) Inverse FFT of the masked Fourier Transform, highlighting the ordered regions.

Fig. 5 (a) Scheme of the atomistic model used in the HAADF-STEM simulations. (b) HAADF-STEM simulated images for different t values. (c) Intensity profiles (integrated in the highlighted regions in (b)) along the $[110]$ direction in the simulated HAADF images, showing the evolution of the apparent ordering degree as a function of thickness (t).

4 Conclusions

In this work we have shown the ordering and microstructure of GaInP layers grown with different amounts of Sb/P ratio in the gas phase during the epitaxial growth by MOVPE on Ge(001) substrates with 6° misorientation towards the nearest $[111]$. The type of ordering observed is CuPt_B single variant and it is unaffected by the use of Sb during the epitaxial growth, as shown from electron diffraction and HAADF data. The relative intensities of the $(h \pm 1/2, k \mp 1/2, l \pm 1/2)$ satellite spots related to the order became weaker with increasing Sb flux, in good agreement with the reduction of the order parameter as determined from previous PL measurements. The extension angle of the APBs also increases with the Sb/P ratio. GaInP ordering has been revisited by atomic resolution aberration corrected STEM-HAADF imaging in combination with HAADF image simulations. The extinction of Z-contrast in APB is discussed in terms of relative thickness of overlapping ordered domains.

5 Acknowledgments

This work has been supported by the European Commission by means of the LONGESST Project under grant agreement 607153, by the Spanish Ministerio de Economía y Competitividad through the projects TEC2014-54260-C3-1-P, PCIN-2015-181-C02-02, MAT2013-41506 and MAT2016-79455-P, MAT2016-79455-P and from Madrid local government under contract S2013/MAE-2780 (MADRID-PV).

The technical assistance of Jesús Bautista and the École Central de Paris for the use of the aberration corrected Titan instrument are also acknowledged.

References

- 1 P. Bellon, J. P. Chevalier, G. P. Martin, E. Dupont-Nivet, C. Thiebaut and J. P. Andre, *Appl. Phys. Lett.*, 1988, **52**, 567.
- 2 A. Gomyo, T. Suzuki and S. Iijima, *Phys. Rev. Lett.*, 1988, **60**, 2645–2648.
- 3 P. Bellon, J. P. Chevalier, E. Augarde, J. P. André and G. P. Martin, *Journal of Applied Physics*, 1989, **66**, 2388.
- 4 J. M. Olson, W. E. McMahon and S. Kurtz, *4th IEEE World Conference on Photovoltaic Energy Conversion*, 2006, **1**, 787–790.
- 5 G. B. Stringfellow, J. K. Shurtleff, R. T. Lee, C. M. Fetzer and S. W. Jun, *J. Cryst. Growth*, 2000, **221**, 1–11.
- 6 S. H. Lee, C. Y. Fetzer, G. Stringfellow, D. H. Lee and T. Seong, *J. Appl. Phys.*, 1999, **85**, 3590.
- 7 S. W. Jun, R. T. Lee, C. M. Fetzer, J. K. Shurtleff, G. B. Stringfellow, C. J. Choi and T.-Y. Seong, *J. Appl. Phys.*, 2000, **88**, 4429.
- 8 C. S. Baxter, W. M. Stobbs and J. H. Wilkie, *J. Cryst. Growth*, 1991, **112**, 373–385.
- 9 E. Dobrocka, I. Vavra and L. R. Wallenberg, *J. Appl. Phys.*, 2001, **89**, 2653–2664.
- 10 G. Hahn, C. Geng, P. Ernst, H. Schweizer, F. Scholz and F. Phillipp, *Superlattice Microst.*, 1997, **22**, 301–305.
- 11 Y. Ohno, *Jpn. J. Appl. Phys.*, 2006, **45**, 2357.
- 12 L. C. Su, I. H. Ho and G. B. Stringfellow, *J. Appl. Phys.*, 1994, **75**, 5135.
- 13 P. Ernst, C. Geng, G. Hahn, F. Scholz, H. Schweizer, F. Phillipp and A. Mascarenhas, *J. Appl. Phys.*, 1996, **79**, 2633.
- 14 T. Y. Seong, J. H. Kim, Y. S. Chun and G. B. Stringfellow, *Appl. Phys. Lett.*, 1997, **70**, 3137–3139.
- 15 Y. Ohno, *Physica B*, 2006, **376-377**, 845–848.
- 16 H. M. Cheong, A. Mascarenhas, S. P. Ahrenkiel, K. M. Jones, J. F. Geisz and J. M. Olson, *J. Appl. Phys.*, 1998, **83**, 5418.
- 17 L. Chernyak and A. Osinsky, *Appl. Phys. Lett.*, 1997, **70**, 2425.
- 18 S. P. Najda, A. Kean and G. Duggan, *J. Appl. Phys.*, 1997, **82**, 4408–4411.
- 19 M. Wu, E. Luna, J. Puustinen, M. Guina, A. Trampert, M. Wu, E. Luna, J. Puustinen, M. Guina and A. Trampert, *Applied Physics Letters*, 2014, **105**, 041602.
- 20 E. Barrigón, B. Galiana and I. Rey-Stolle, *J. Cryst. Growth*, 2011, **315**, 22–27.
- 21 E. Barrigón, L. Barrutia and I. Rey-Stolle, *J. Cryst. Growth*, 2015, **426**, 71–74.
- 22 R. T. Lee, C. M. Fetzer, S. W. Jun, D. C. Chapman, J. K. Shurtleff, G. B. Stringfellow, Y. W. Ok and T. Y. Seong, *J. Cryst. Growth*, 2001, **233**, 490–502.
- 23 S. P. Ahrenkiel and M. C. Hanna, *Appl. Phys. Lett.*, 2001, **79**, 1781–1782.
- 24 S. Takeda, Y. Kuno, N. Hosoi and K. Shimoyama, *J. Cryst. Growth*, 1999, **205**, 11–19.
- 25 H. Murata and I. H. Ho, *Appl. Phys. Lett.*, 1995, **67**, 3747.