On the Use of Sb to Improve the Performance of GaInP Subcells of Multijunction Solar Cells

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Abstract — GaInP is a material commonly employed for the top subcells of different multijunction solar cells architectures. In this study, the performance of GaInP top cells has been improved by increasing the energy band gap with the use of Sb as a surfactant during the MOVPE growth of the structures. The optimization of the appropriate Sb molar flow was done by Reflectance Anisotropy Spectroscopy. Different characterization techniques have been employed to assess the effect of Sb on the morphology, microstructure and optoelectronic properties of the resulting GaInP grown with different Sb/P ratios. Finally, the performance of several GaInP subcells with different order parameters has been assessed.

Keywords — GaInP, Sb, surfactant, External Quantum Efficiency.

I. INTRODUCTION

A certain diversity of multijunction solar cell (MJSC) architectures has already demonstrated a great potential for ultra-high efficiency (i.e. upright metamorphic [1], inverted metamorphic [2], MJSCs using bifacial epigrowth [3], MJSCs using wafer bonding [4], [5]). However, such diversity mostly affects the middle and/or bottom cell composition and structure, remaining GaInP as the material of choice for the top cell (TC). Therefore, being able to maximize the performance of GaInP top cells is a need for almost all multijunction solar cell approaches. In this optimization context, addressing the ordering phenomena exhibited by GaInP, appears as a fundamental issue to be tackled.

GaInP, as many other III-V ternaries, shows CuPt ordering in the group III sublattice. CuPt-type ordering describes a superlattice of alternating GaInP atomic layers with structure $Ga_{0.5(1-\eta)}In_{0.5(1+\eta)}P/Ga_{0.5(1+\eta)}In_{0.5(1-\eta)}P$, where η is defined as the order parameter. For a completely disordered GaInP material $\eta=0$, whereas for a completely ordered material $\eta=1$. So far, only experimental values as high as $\eta=0.6$ have been reported for GaInP grown in MOVPE [6, 7].

The degree of order modulates, among others, the energy bandgap (E_g) of the alloy [8]. In order to increase the conversion efficiency of a MJSC, the energy band gap of the GaInP TC should be increased as much as possible [9] or, in other words, to have a disordered GaInP TC. In fact, as much as a 160 meV increase in E_g (at low T) has been reported after decreasing the ordering degree [10]. In order to control the degree of order, either epitaxial growth parameters (such as growth temperature,

growth rate, V/III ratio, doping level, wafer off cut) [11-15] are changed, or surfactants are employed during the epitaxial growth [16].

In MOVPE growth, three different elements have been identified so far as surfactants on GaInP, namely, Te, Bi and Sb. However, Sb is the best candidate to be used during the growth of a GaInP-based solar cell [16], since Te is a n-type dopant on GaInP with a strong memory effect [17] and Bi deteriorates the surface morphology and might form compounds such as BiAs and BiP [18]. In addition, Sb is isoelectronic with P (i.e., it will not affect the Fermi level position) and the incorporation of Sb in the solid is low, namely around $1 \cdot 10^{18}$ cm^{-3} [19]. As an important drawback, if excessive Sb is used, the resulting GaInP layer will exhibit composition modulation and a triple period order which, in turn, notably lowers the value of E_g [18, 20]. In this paper, we first assess the effect of Sb on the morphology, structure and bandgap of single GaInP layers. Subsequently, we employ different Sb flows during the growth of GaInP solar cells and analyze the spectral response of the resulting devices.

II. EXPERIMENTAL

Samples were grown in a horizontal commercial MOVPE reactor (Aixtron AIX200/4) equipped with an in situ RA spectrometer (Lay Tec EpiRAS 200). We used Ge (100) substrates with 6° misorientation towards [011] direction, TESb was used as the Sb precursor, and growth temperature was 675°C.

Sb flow was optimized with the use of specific calibration structures consisting of a GaInP nucleation layer (365 nm thick) on a Ge substrate followed by a 1.1 μm thick, Zn-doped, GaInP layer where different specific molar flows of Sb were introduced. These calibration structures were characterized by means of photoluminescence (PL), atomic force microscopy (AFM), and transmission electron microscopy (TEM) measurements. PL was performed at room temperature by exciting the GaInP layers with a 532 nm laser. For the AFM, Digital Instruments-Multimode IIIa microscope working in tapping mode was used and the resulting AFM scans were processed using a free software tool [20]. For the TEM characterization, samples were thinned down to electron transparency using a Focus Ion Beam (FIB) lift out technique and then a JEOL 2100 and an aberration corrected Titan FEI

operated a 200kV for conventional TEM and high resolution analyses, respectively.

GaInP solar cells on Ge substrates were also grown. The detailed semiconductor structure can be found in Ref [21]. In essence, the GaInP solar cell consists of an n-type emitter doped with Si ($\sim 1 \cdot 10^{18}$ cm^{-3}) and p-type base doped with Zn ($\sim 1 \cdot 10^{17}$ cm^{-3}). As the photogeneration of carriers in our solar cell configuration takes mainly place in the TC-base, disordering of the TC-base is mandatory. Therefore, the study of the use of Sb was done mainly on the p-type GaInP layers.

The effective change in the energy bandgap was evaluated with External Quantum Efficiency (EQE) measurements. EQE set-up is based on a Xenon lamp used as a white light source, together with a Horiba Jobin Yvon monochromator (TRIAX 180) and a filter wheel. The monochromatic light was chopped at a frequency of 481 Hz. A current preamplifier (SR570) was used to convert the output currents into voltage that was measured by a two channel lock-in amplifier (Anfatec 203).

III. RESULTS

A. In situ calibration of the Sb/P molar flow ratio to disorder GaInP

The first step to control the degree of order of GaInP with Sb is thus to precisely determine the Sb molar flow that has to be introduced during the growth of GaInP in the reactor chamber to achieve a desired order parameter [16]. In our case, this was calibrated in situ with RAS. Since it is intended that Sb acts as a surfactant –and thus it does not significantly incorporate into the semiconductor lattice–, its molar flow should be rather low. Additionally, the appropriate molar flow lies within a given range to get the desired surfactant effect (i.e., to get a disordered GaInP layer). Below this range no effect is expected, whereas above, the previously commented triple period ordering is induced .

The Sb molar flow that should be applied varies from the different reactor conditions, reactor geometry, growth T and V/III ratio [16, 22, 23, 24]. Here, we have employed RAS to determine the adequate molar flow that is necessary to get Sb as a surfactant. For this purpose, a GaInP layer was grown on a Ge substrate. Once the growth was finished, the sample was kept at growth temperature under a constant PH$_3$ molar flow, and then a certain Sb molar flow was introduced in the reactor chamber and, after some stabilization time, the RAS spectra of the Sb-exposed surfaces were taken. This process was repeated for different Sb/P ratios. Fig. 1 shows how the RAS signal at 3 eV is affected by varying the Sb/P ratio. According to the results shown in Fig. 1, the adequate Sb/P range that potentially will modulate the order parameter of GaInP grown at 675°C was found to be in a range between 411 to 1720 ppm [25].
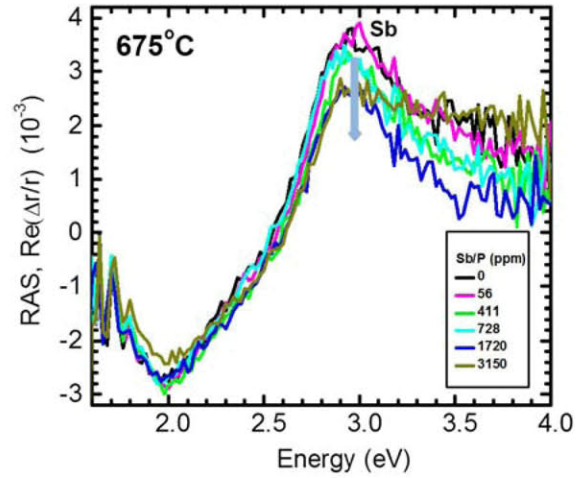

Fig. 1.   In situ RA spectra of a GaInP surface under different ratios of Sb/P taken at 675°C.

B. Characterization of the properties of GaInP:Sb layers

Once it was identified the appropriate range of Sb/P ratio to be used, several GaInP layers were grown within the range determined by RAS.

Preliminary PL measurements performed at RT on both n-type and p-type test GaInP layers (Fig. 2(a)) indicated that the n-type GaInP emitter was almost disordered (peak at 1.89 eV) while p-type GaInP was still partly ordered (peak at 1.82eV) In addition, from the layers grown with different Sb/P ratios, it can be observed (Fig. 2(b)) how the peak position shifts to higher energies as the amount of Sb is also increased, ranging from 1.819 eV up to 1.884 eV. Such high E$_g$ value (low ordering) is compared to the PL peak transition (Fig. 2(a)) obtained for the n-type Si doped GaInP emitter described before. These PL results confirm the suitability of RAS to determine the adequate Sb/P ratios for a given reactor and growth conditions.

The morphology of the layers is also affected by the use of Sb. Fig. 3 shows 4×4 µm AFM topography scans (both with the same Z scale) of two GaInP samples with different Sb molar flows. For the sample shown in Fig. 3(a) an Sb/P ratio of 411 ppm was used, while for the sample in Fig. 3(b) was 1721 ppm. The RMS roughness values are 2.54 and 1.82 nm, respectively. In addition, samples were analyzed by TEM. The high quality of the samples is illustrated in bright field images (Fig. 4(a)). Selected area diffraction patterns (SAED) in cross section along the [110] zone axis of the samples were also recorded. For the sample grown with no Sb (Fig. 4(b)) the presence of extra diffraction spots —indicating the presence of a superlattice— are clearly observable. As long as the Sb/P ratio is increased, they become less bright until they are not detectable anymore in the diffraction pattern (Fig. 4(c)). This observation confirms the results obtained with PL in Fig. 2(b).
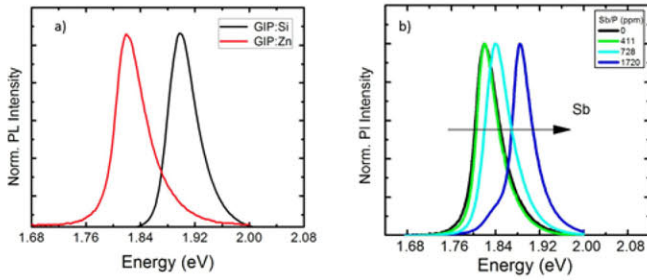
Fig. 2. (a) Normalized PL measurements at RT of two different test GaInP layers grown under the same conditions of the TC base (red) and TC emitter (black). Fig. 2. (b) Normalized PL measurements at RT of GaInP TC base layers with different amounts of Sb.
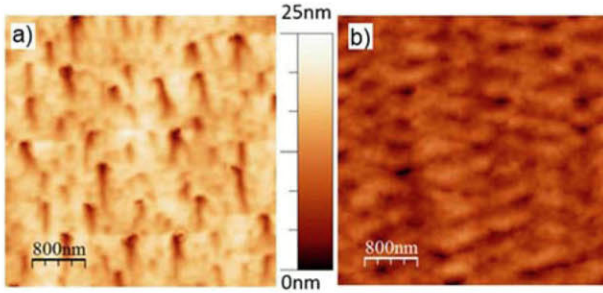

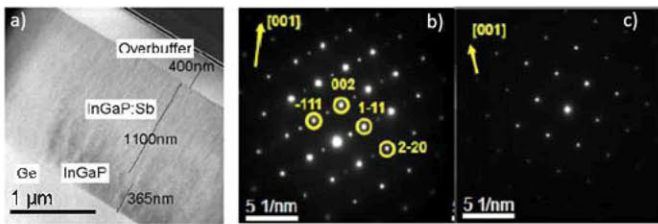Fig. 3. AFM images for GaInP layers with Sb/P ratio of 411 ppm (a) and 1721 ppm (b).

Fig. 4. a) Bright field image of one GaInP calibration sample. Fig. 4. (b) Transmission diffraction patterns along the [110] zone axis of the GaInP layers grown with no Sb and with an Sb/P ratio of 1720 ppm (c).
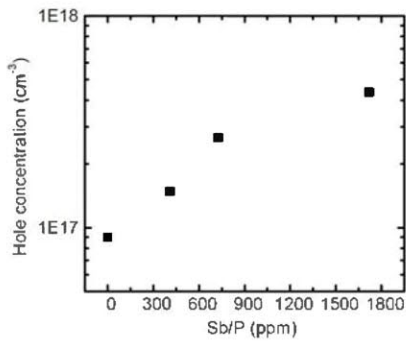

Fig. 5. Hole concentration versus different Sb/P ratios.

Another important fact that must be also taken into account for the final solar cell devices, is that the Zn incorporation is enhanced as the Sb/P ratio is increased [16, 26]. Doping concentration was measured for the different GaInP layers confirming this effect (Fig. 5). It can be seen how the concentration is increased by a factor of 4 for the Sb/P ratio range explored.

C. Characterization of GaInP top cells with different order degree

Once the use of Sb has been optimized to obtain GaInP layers with different degree of order, an assessment of the use of Sb on the performance of GaInP solar cells has been carried out. Several GaInP solar cells have been grown using different Sb/P ratios in the top cell base.
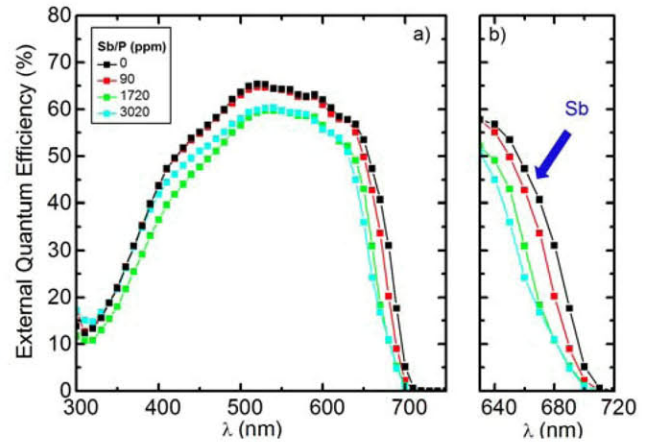

Fig. 6. EQE measurements of GaInP solar cells with different Sb/P ratios.

Fig. 6 shows the EQE of the resulting cells with different Sb/P ratios. Notice that no antireflection coating layers (ARC) were deposited. As can be observed, the cut-off wavelength of the cell is effectively decreased with the use of Sb, which is indicative of the achievement of higher band gaps. The difference observed in the values of the EQEs are due to the change in the effective doping of the base (Fig. 5),which has not been correctly counterbalanced by reducing the dopant flow. According to these results, adequate Zn incorporation in the base should be achieved in order to realize a more realistic comparison of the EQE results. This work is currently on going.

In addition, an increase of 60 mV in the open circuit voltage (V_{oc}) of the devices grown with Sb has been achieved. Obviously, this increase in V_{oc} depends on the initial degree of order before Sb introduction. According to our simulations, this V_{oc} increase could imply an efficiency increase of 0.75% absolute in a lattice-matched GaInP/Ga(In)As/Ge triple junction solar cell.

Moreover, further experiments are ongoing to ascertain the changes in the spectral response of the GaInP TC when different amounts of Sb are also introduced during the growth of the Si-doped GaInP emitter that is already largely disordered.

IV. SUMMARY

In this work an effective change in the band gap GaInP solar cell has been demonstrated by the use of Sb during its growth. RAS has been applied to determine the proper molar flow of Sb that must be introduced to induce a change in the order degree. A complete morphological, structural and optical characterization has been accomplished to the resulting GaInP:Sb layers.

Several GaInP solar cells have been grown with different Sb/P ratios. An effective change in the energy bandgap has been observed in the EQE measurements. A V_{oc} increase of 60 mV has been also measured.

REFERENCES

[1] King RR, Law DC, Edmondson KM, Fetzer CM, Kinsey GS, Yoon H, Sherif RA, Karam NH, "40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells" Applied Physics Letters 90 , 18 (2007).

[2] Geisz JF, Friedman DJ, Ward JS, Duda A, Olavarria WJ, Moriarty TE, Kiehl JT, Romero MJ, Norman AG, Jones KM. "40.8% efficient inverted triple-junction solar cell with two independently metamorphic junctions", Applied Physics Letters 93 123505-1 (2008).

[3] P. Chiu, S. Wojtczuk, X. Zhang , C. Harris C, D. Pulver, M. Timmons. "42.3% efficient InGaP/GaAs/InGaAs concentrators using bifacial epigrowth", in Photovoltaic Specialists Conference (PVSC), 2011 37th IEEE, 000771–000774(2011).

[4] F. Dimroth et al. "Wafer bonded four-junction GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency" Progress in Photovoltaics Research and Applications 22, 277-282 (2014).

[5] Friedman, D. J. "Progress and challenges for next-generation high-efficiency multijunction solar cells." Current Opinion in Solid State and Materials Science 14(6): 131-138 (2010) .

[6] P. Ernst , C. Geng,F.Scholz, H. Schweizer, Y.Zhang and A. Mascarenhas, Appl. Phys. Lett. 67, 2347 (1995).

[7] S. H. Lee and C. M. Fetzer, G.B. Stringfellow, C.J. Choi, and T.Y. Seong,J. Appl. Phys. 86, 1982 (1999).

[8] A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. 60, 2645(1988).

[9] S. R. Kurtz, P. Faine, and J. M Olson,, J. Appl. Phys. 68.4, p.1890 (1990).

[10] L. C. Su , I. H. Ho, N. Kobayashi and G.B Stringfellow, J. Cryst. Growth 145, pp. 140 –146, (1994).

[11] H. Murata, I. H. Ho, Y. Hosokawa, and G. B. Stringfellow,Appl.Phys. Lett. 68, 2237 (1996).

[12] H. Murata, I. H. Ho, L. C. Su, Y. Hosokawa, and G. B. Stringfellow, J. Appl. Phys. 79, 6895 (1996).

[13] H. Murata, T. Hsu, I. Ho, L. Su, Y. Hosokawa, and G. Stringfel low, Appl. Phys. Lett. 68, 1796 (1996).

[14] S. R. Kurtz, J. M. Olson, and A. Kibbler, Appl. Phys. Lett.57,1922 (1990).

[15] I. García, I. Rey-Stolle, C. Algora, W. Stolz, and K. Volz, "Influence of GaInP ordering on the electronic quality of concentrator solar cells", J. Cryst. Growth 310, 5209 (2008).

[16] J. Olson, W. McMahon, and S. Kurtz, "Effect of Sb on the Properties of GaInP Top Cells," Conference Record of the 4th World Conference on Photovoltaic Energy Conversion, vol.1, no., pp.787,790, May 2006.

[17] G. Stringfellow, J. Shurtle, R. Lee, C. Fetzer, and S. Jun, "Surface processes in OMVPE–the frontiers", J.Cryst. Growth 221, 1 (2000).

[18] S. Lee, C. Fetzer, and G. Stringfellow, "Effect of Te doping on step structure and ordering in GaInP", J. Cryst. Growth 195, pp. 13-20 (1998).

[19] J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and G. B. Stringfellow, "Band-gap control of GaInP using Sb as a surfactant", Appl. Phys. Lett. 75, 1914 (1999).

[20] I. Horcas , R. Fernández , J.MGómez-Rodríguez , J. Colchero , J. Gómez-Herrero J and Baro, "WSXM: A software for scanning probe microscopy and a tool for nanotechnology" Rev. Sci. Instrum. 78 013705 (2007).

[22] C. M. Fetzer, R. T. Lee, J. K. Shurtle_, G. B. Stringfellow, S. M Lee, and T. Y. Seong, Appl. Phys. Lett. 76, 1440 (2000).

[21] E. Barrigón; E. García-Tabarés, I. García, I. Rey-Stolle, C. Algora, "Triple-junction solar cells for ultra-high concentrator applications". Spanish Conference on Electron Devices,1-4, (2011).

[23] R. Lee, J. Shurtleff, C. Fetzer, G. Stringfellow, S. Lee, and T. Seong, "Surfactant controlled growth of GaInP by organometallic vapor phase epitaxy", J. Appl. Phys. 87 (8), pp. 3730-3735 (2000).

[24] T. Y. Seong, S. M. Lee, R. T. Lee, and G. B. Stringfellow, "Isoelectronic dopant induced ordering transition in GaInP grown by organometallic vapour phase epitaxy" Surf.Sci. 457, L381-L385 (2000).

[25] E. Barrigón, L. Barrutia, I. Rey-Stolle, "Optical in situ calibration of Sb for growing disordered GaInP by MOVPE", Journal of Crystal Growth, (in press) DOI:10.1016/j.jcrysgro. (2015.05.020).

[26] D. Chapman, A. Howard, and G. Stringfellow, "Zn enhancement during surfactant mediated growth of GaInP and GaP", J. Cryst. Growth 287, pp. 647(2006).