Study of Metal Organic Chemical Vapour Deposition (MOCVD) semiconductors III-V hyperstructures with Secondary Ion Mass Spectrometry (SIMS).

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Abstract. One of the most promising technologies in high efficiency solar cells is based on quaternary structures grown by epitaxial techniques as Metal Organic Chemical Vapour deposition (MOCVD). The semiconductors III-V structures are elaborated under tailored parameters, allowing the use of a broader area of the solar spectrum. Analytical techniques capable of providing accurate and precise information in cross sections about the composition and thickness of the layers are demanded. Secondary Ion Mass Spectrometry (SIMS) has been used for characterization of these structures due to its high depth resolution and sensitivity, stability and reproducibility. It was detected the diffusion process of Al and In across the cell interfaces and the layer diffusion over GaAs substrates. The Al diffusion was associated at incorrect incorporation of elements during growth process and the layer diffusion was associated at changes of manufacturing parameters. Such studies show the SIMS ability to diagnose of faults during the growth process, detection of impurities and incorrect diffusion of dopants that may affect the layer properties and the structure functionality.

1. Introduction
In the cell solar industry, silicon solar modules account a high portion of the market despite its moderate efficiency in the use of the whole solar spectrum. Due to this fact, a concentration device is commonly incorporated to improve its conversion efficiency [1-3]. However, it may cause the increase of the cell temperature with the solar exposition and the reduction in cell efficiency. Since 1980s, solar cells based in structures composed by layer of III-V semiconductors materials have been studied. They exhibit a direct band gap with tuneable absorption zone and allow the efficient use of the whole solar spectrum [4]. Although III-V solar cells have been considered too expensive because of the raw materials and processes involved in their production; the combination of these structures with the PV technology assures high efficiency with respect to conventional silicon solar cells [1]. Besides, the use of Ge substrates allows the manufacturing of thinner and lighter structures. These characteristics have made these solar cells the choice for space applications as the higher power–weight ratio permits to reduce weight and consequently reduce launch costs [5]

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The manufacturing solar cell industry requires analytical tools to study the fabrication process and properties in cross sections at high resolution, check the interface regions and detect diffusion processes between substructures or incorrect growing process of layers that can degrade the solar cell efficiency [2-7]. SIMS has shown to be a sensitive technique for studying the distribution of dopants and contaminants over these materials, due to the complete atomic/molecular information provided and its excellent sensitivity and reproducibility. The cited characteristics allow to determine manufacturing defects or diffusion processes that can affect its functionality or the physical layer properties [2,3,6]. In this paper, a study of the diffusion process in III-V semiconductor structures is presented, SIMS has been used for to characterize and study the structures become a diagnostic tool for elaboration process.

2. Experimental Setup
A solar cell structure (GaInP/InGaAs/Ga(In)As/Ge) consists of three subcells GaInP/Ga(In)As/Ge connected with tunnel junction (TJ) and are grown on a 140 µm thick Ge wafer by MOCVD. An operative cell shows specific values of structural, electrical and optical parameters that allow to obtain the best performance; defective cells don’t show it. The efficiency of the cell is degraded by the surface defects, diffusion across the interfaces or misfit dislocations [2-7]. SIMS has been used to study and characterize a complete and operative structure (GaInP/InGaAs/Ga(In)As/Ge) with Ar ions [2], the analysis conditions were optimized to obtain good depth-resolution without compromising either the sensitivity or the reproducibility of the analysis. In this paper, a fully-operative cell (sample A) and a defective one (sample B) were studied under identical sputtering conditions as reported [2] but using O₂⁺ to increment the sputtering rate. It has been studied if there are differences in layer composition or layer distribution of the samples that can be associated at its functionality. The signal SIMS corresponding to 27Al⁺, 28Si⁺, 31P⁺, 64Zn⁺, 69Ga⁺, 75As⁺, 115In⁺ and 74Ge⁺, elements presents in the structure were monitored.

In other hand, It was analysed the influence in the layer structure of the gas flow of the organic compounds in the MOCVD reactor during growth process. It was used a set of simple structures grown over GaAs substrate. The samples were elaborated keeping the parameters similar at the cells manufacturing parameters, except Ga flow. In the Table 1 is shown the gas flow values of the different elements in the growth process of samples. The signal SIMS corresponding to 27Al⁺, 31P⁺, 69Ga⁺, 75As⁺ and 115In⁺ were monitored.

| Sample | Element | 1 | 2 | 3 | 4 | 5 |
|--------|---------|---|---|---|---|---|
|       | Al      | 52.00 | 52.00 | 52.00 | 52.00 | 52.00 |
|       | Ga      | 44.00 | 49.50 | 44.68 | 44.36 | 45.00 |
|       | In      | 440.00 | 440.00 | 440.00 | 440.00 | 440.00 |
|       | PH₃     | 1200.00 | 1200.00 | 1200.00 | 1200.00 | 1200.00 |
3. Result and discussion

3.1. Structure identification

For the optimization process, a complete positive SIMS mass spectrum was recorded on different interfaces of the complete operative structure for to determine both the species in the sample and possible interferences (mass spectra do not showed here). The basic structure of the operative cell was reported previously [2], the diverse substructures have been identified by meaning of the intensity variations of the main elements across the interfaces.

Figure 1 shows the depth profile of the complete and operative structure, with the signal intensity of each element normalized. The different substructures and interfaces between subcells (GaInP/Ga(In)As/Ge) in a operative cell, are marked in the figure with dot lines.

![Figure 1. In-depth SIMS analysis of structure similar at operative triple junction solar cell, obtained with O²⁺ ions in positive mode. Subcells and Tunnel Junctions (TJ) are marked with dot lines.](image)

3.2. Study of Diffusion process between interfaces

As mentioned, an operative cell has physical, morphological and optical properties with specific values and must exhibit clear interfaces between the layers of the different structures. In a SIMS depth profile, the interfaces are detected by the variations in signal intensity of the principal elements. Figure 2 exhibits a zoom of the depth profile of the top cell and TJ (Tunnel Junction) zones in samples A and B. Sample A exhibits interfaces between the subcells clearly. The InGaAs/GaAs interface (t= 14.28 min) is identified by the reduction of In and increment in Ga and As. The GaAs/AlInP interface (t=15.30 min) is determined by the meaning the increment of Al, In and P. In general, in sample B is observed a displacement in the sputtering times, as well as blurred interface zones, evidencing some Al diffusion over the InGaAs/GaAs and AlInP/GaInP interfaces. Although the interface GaAs/AlInP (t=13.20 min) in sample B appears at the same sputtering time than in sample A, the Al signal is observed last longer than in the sample A and the structure is observed enlarged.
Figure 2. Detail zoom of the in-depth analysis of hyperstructure corresponding of top cell Sample A (left) and Sample B (right): contact layer (GaAs/InGaAs), window (AlInP) and emitter (GaInP). Main elements: Ga (solid line), In (grey), P (triangles), As (circles), Al (dashed) and Ge (squares).

Figure 3 shows the depth profile of interfaces between the top and middle cell in sample A and B. Again, significant differences are observed in the defective cell depth profile. In Sample B profile the AlGaInP and GaAs/AlGaAs layers are significantly thicker than in the operative cell, is indicating by the lack of the bump in the In signal and the much broader diffusion of Al. Diffusion processes are also observed in the interface between top and middle subcell, the interfaces are not clearly defined and the sputtering times are modified. The diffusion of Al and In on next substructure blurring the interfaces AlGaInP/GaAs/AlGaAs, in a similar process observed over the upper section (Figure 2). Similar behaviour is detected in the union between the middle and bottom cell, it is shown in figure 4. In sample A (Figure 4 left), the GaInP/AlGaInP interface is observed at t=130 min, the AlGaInP/GaInAs interface is detected at t=140 min. In the sample B (Figure 4 right) GaInP/AlGaInP interface appears at 128.5 min, the AlGaInP/GaInAs interface is detected at t=150 min; its observed Al diffusion over the bottom cell and the In and As profiles are enlarged and undefined.

The interaction of the sample with the sputtering primary ions can be result in small diffusion in the samples or ion implantation [6]. Diffusion processes are not observed in sample A where the structures are clearly defined while in the sample B it causes enlargement of the structures and degradation of the interfaces. The causes of variation of the sputtering times of sample B, with respect at sample A, are not totally understood. Based on the results, SIMS analysis suggests that the diffusions observed in the sample B are a consequence of the manufacturing process causing defects in the sample. It have been reported the mutual diffusion and atomic exchange of species at the heterointerfaces (InGaP/GaAs) [5], As diffusion over InGaP layers grown with MOVPE [7] and the interdiffusion of Al in thin structures [8]. All these processes smooth out the interface abruptness and degrade device performance. We assumed, in agree with the literature and SIMS analysis, that the incorrect incorporation of Al and In at the structure during growth process cause the observed inter-diffusion process and affects at the rest of element profiles, causing degradation and reducing the quality performance of the sample B.
3.3. Influence of fabrication parameters
SIMS allows study the influence of the changes in the growth conditions in the structure composition and properties. Changes in the reactor flows during the growth process cause variations in the structure, dopants distribution and the cell performance [4]. It was studied a set of simple structures grown over GaAs substrate. SIMS analysis was made in positive mode, with Ar⁺ ions and current of 580 nA following the procedure described in [2]. The in-depth profiles of samples are similar for all samples and there are not apparent differences between samples (Figure 5). Ga and As signal are stable at t=14 min, indicating the reaching of the substrate.
Normalization to an internal reference element facilities the direct comparison of different profiles, assuming the same material and properties and allows the determination of differences between the samples [6]. Considering the samples, Al is selected as its growing parameters were not changed in any of the samples, and its SIMS signal is high. The performance of SIMS signal to reveal differences in the growth layers as a consequence of changes in the manufacturing process may be seen in figure 6. As seen in the interface layer/substrate (t=11 min), there are changes in the sputtering time and in the slope of the signal. Sample 2 (with a higher flow of Ga during the growing process) shows a higher sputtering time and its slope is sharper than the other samples (Figure 6 right). The variation in the sputtering rate could indicate that the layer physical properties have been modified and that the layer diffusion over substrate is reduced with an increment in the Ga flow.

**Figure 5.** In depth-analysis of basic structure over GaAs substrate. Main elements: Ga (solid line), In (grey), P (triangles), As (circles) and Al (dashed).

**Figure 6.** In-depth analysis of Ga signal normalized with respect at Al signal of samples: S1, S2 y S5. Left: Zoom of Layer zone. Right: Zoom of interface zone.

4. Conclusions
SIMS has been used like to study triple junction solar cells and other simple structures grown by MOCVD. With the elemental depth profile (Ga, As, In, Al, P and Ge) allow the clear identification and assignment of the substructures and the functional layers in an operative cell. The depth profile of defective cell shown diffuse interfaces between layers and blurring the structure, it can be associate at inter-diffusion caused by the incorrect incorporation of Al and In at the structure or failures in the process during growth process. The influence of the manufacturing parameters in the layer properties has been studied in simple structures, and it is determined that the changes in the gas flow of organic compounds in the MOCVD reactor can cause variations in the layer diffusion or layer properties. The SIMS capacity for detect diffusion or incorrect incorporation of elements in the complete hyperstructure and detect failures during the manufacturing process has been established. SIMS has
demonstrated to be an extremely sensitive tool to evaluate the growth process in a different type of hyperstructures.

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Corrigendum

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The author and affiliations were not produced in the correct order in the original article. The correct order is below.

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