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Abstract. The Multijunction (MJ) monolithic approach is very attractive for a competitive concentrating photovoltaic (CPV) technology; it has been successfully applied for InGaP/GaInAs/Ge triple-junction structures but it is more difficult to be exploited for manufacturing 4-junction solar cells, in particular when III-V and IV elements are both used. So far, the integration of the 1 eV SiGeSn material in the lattice-matched InGaP/GaInAs/Ge triple-junction structure has required the utilization of two different growth apparatus, nearly losing the economic advantage of the monolithic architecture, owing to the related higher capital expenditure. The central technical challenge for realizing InGaP/GaInAs/SiGeSn/Ge solar cell at low cost, with an industrial approach, lies in the growth of III-V and IV elements in the same MOVPE equipment, by solving the "cross contamination" problem among the III-V elements and the IV elements. In this contribution, for the first time, the results of the investigation concerning the growth of SiGe(Sn) and III-V compounds in the same MOVPE growth chamber are presented. The epitaxial layers have been characterized by XRD, SEM, TEM, EDX, SIMS and ECV profiling. It is eventually shown that by starting from a modification of the MOVPE equipment and by setting up proper growth condition the contamination of III-V elements in IV based materials can be drastically reduced from 10^{20} cm^{-3} to $2*10^{17}$ cm^{-3}, while the contamination of IV elements in III-V compounds can be reduced from $4\text{-}5*10^{17}$cm^{-3} to $6*10^{16} - 3*10^{14}$ cm^{-3} depending on the substrate used.

INTRODUCTION

In order to increase the efficiency value of III-V based multijunction (MJ) solar cells, three main technological approaches are under development: the monolithic [1], the mechanically stacked [2] and the wafer bonded [3]. The first one is the most attractive from an economical point of view, however it suffers of un important constrain: the need of utilizing different semiconductor materials with the same lattice constant. So far the most "popular" device realized with this approach is the triple junction (TJ) InGaP/InGaAs/Ge solar cell, which has reached un efficiency value slightly over 40% [4]. A promising path towards the manufacturing of higher efficiency monolithic 4-junction solar cells has been proposed by integrating in the mentioned TJ structure a semiconductor material with un energy gap around 1 eV and with a lattice constant equal to Ge [5]. Dilute nitrides have been first discovered to satisfy these requirements, even if the MOVPE solar cells realized with these materials demonstrated low quantum efficiency values [6], [7]. Among the solutions conceived to circumvent this problem, it is worth mentioning the possibility of growing InGaNAs by MBE and then depositing by MOVPE the remaining part of the solar cell structure [8], [9]. These solutions have the drawback of introducing an higher capital cost (CAPEX) for the CPV technology. If the matching constraint is dropped, upright metamorphic four-junction solar cells can be realized by adopting InGaAs as 1 eV material, however this solution requires a careful engineering of the growth process, since crystal defects are inevitably introduced in metamorphic structures [10]. Owing to the fact that its energy gap can be tuned between 0.8 eV and 1.4 eV and it can be grown lattice matched to Ge, SiGeSn has then been considered as an alternative promising 1 eV material [11]. The growth of SiGeSn alloys has been proposed both for MJ and thermophotovoltaic

applications [12]. Furthermore, this ternary material can be used as an intermediate buffer layer to realize monolithic III-V structure on silicon substrate, paving the path for next generation low cost MJ devices [13]. In spite of these encouraging prospective, the most recent integrations of SiGeSn with III-V for MJ solar cells have been accomplished by using two different growth equipment: a CVD reactor for the growth of SiGeSn and a MOVPE growth chamber for the deposition of the remaining part of the cell structure [14], [15]. The reason for such a choice is mostly due to the "cross contamination" among the III-V elements and the IV elements of the periodic table [16]. A key question then arises: may we realize low cost monolithic 4 junction solar cells with III-V and SiGeSn by solving the central technical challenge of growing III-V and IV elements in the same MOVPE reactor?

METHODS

The growth of IV based materials (Ge, SiGe, SiGeSn) and III-V compounds (GaAs, AlGaAs, InGaP, InGaAs) has been carried out in the same growth chamber of an AIX 2800G4 MOVPE "planetary" reactor, with 2 x 4 inch and 6 x 6 inch wafers configuration. The growth chamber is equipped with a "double gas foil rotation" system to facilitate the in-situ control of the temperature profile across the wafers. The standard 2800G4 configuration of the MOVPE reactor has been modified according to the growth results. A special triple gas injector, three independent gas lines for Si, Ge and Sn precursors and a new ceiling set up for a better control of the deposition at low temperature have been implemented. The MOVPE growth has been carried out in N_2 or H_2 carrier gas, in the temperature range 450-640°C. In order to pursue un industrial scale up of the growth process the following gas sources have been used: IBuGe, GeH_4 (10% in H_2), Si_2H_6 (10% in H_2), $SnCl_4$, TMGa, TMIn, PH_3 and AsH_3. The epitaxial layers have been grown on 4 and 6 inch GaAs and Ge substrates and characterized by high resolution X-ray diffraction (HR-XRD), Scanning electron microscope (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray (EDX) analysis. In particular, Secondary Ion Mass Spectroscopy (SIMS) and Electrochemical voltage-capacitance (ECV) have been used to assess the "cross contamination" among the III-V elements and the IV elements.
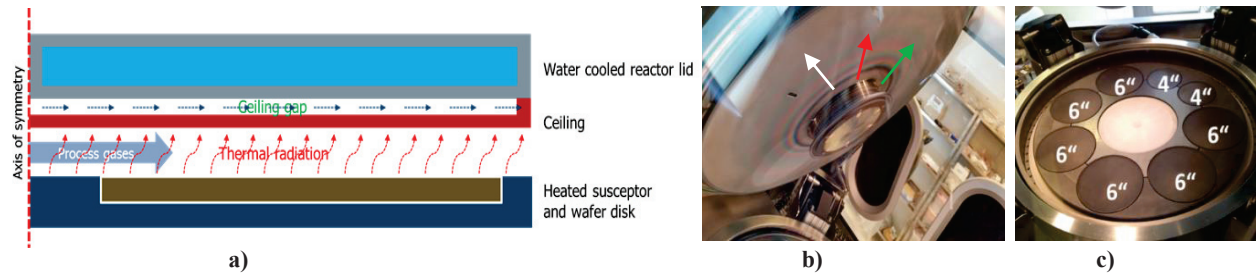
FIGURE 1. a) schematic of the MOVPE growth chamber; b) graphite ceiling and the triple gas injector, c) susceptor and special wafer pocket for an easier process transfer from 4 inch to 6 inch". The area of the ceiling and of the susceptor, which are sources of possible contamination, has been reduced with respect to the standard configuration.

RESULTS AND DISCUSSION

Preliminary test have been carried out on SiGe(Sn) by using IBuGe, Si_2H_6 and $SnCl_4$ in order to understand how to inject the different gases into the reactor chamber, identify proper ceiling temperature and to point out any critical issues owing to the selected gas sources [17]. After the calibration runs performed on Si_xGe_{1-x} , tin has been added in the growth chamber for the deposition of SiGeSn, by keeping almost unchanged the Si amount in the gas phase. The effect of the incorporation of Sn in $Si_{0.026}Ge_{0.974}$ is shown Fig.2. The addition of Sn has the effect of growing SiGeSn slightly in compression both on GaAs and Ge substrates. The solid incorporation of Si and Sn has been evaluated by comparing the measurements performed by HR-XRD and SIMS. These measurements also showed the competitive incorporation of Sn and Si in the ternary material. In spite of the fact that the substrates have similar lattice constant and therefore SiGeSn is expected to find similar strain condition when grown on GaAs and on Ge, very different surface morphologies have been assessed in the two cases. Here we just show part of the structural characterization performed on GaAs substrate, in order put in evidence a critical aspect which characterizes such a growth, when Cl-based precursors are selected.
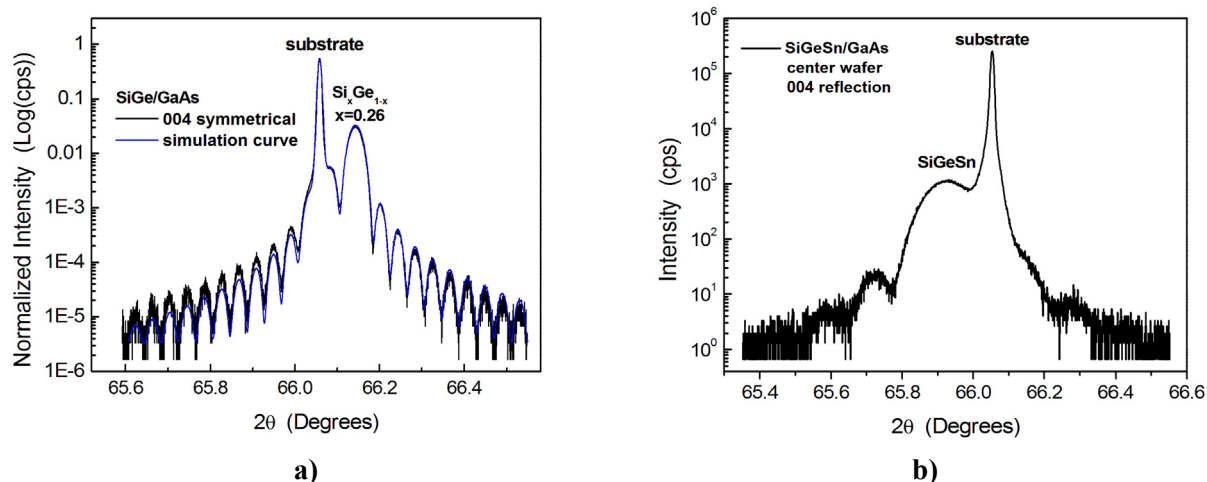
FIGURE 2. ω−2θ HR-XRD curves acquired on a) SiGe grown on GaAs and b) SiGeSn grown on GaAs. The SiGeSn has been growth at 450 °C with a thickness of 150 nm, by keeping almost the same gas phase amount of Si in SiGe.

The growth of SiGeSn on GaAs has been found disturbed by the formation of etch pits. These defects have been attributed to the HCl etching action, since this acid, is likely to be produced in the gas phase trough the chemical reactions involving GeH_4, Si_2H_6 and $SnCl_4$ (Fig.3). We came to the conclusion that for growing SiGeSn on GaAs a suitable intermediate layer has to be deposited in between.
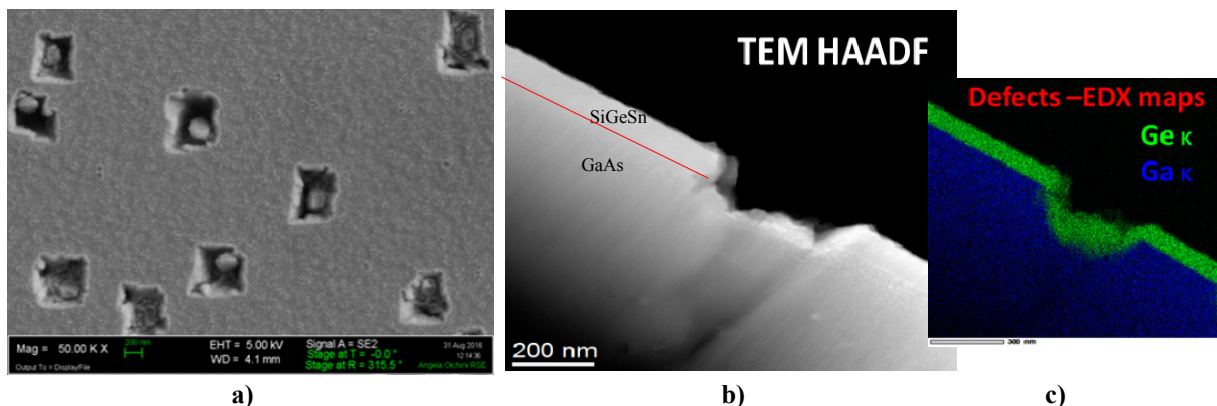
FIGURE 3. a) SEM image and b) TEM image of the SiGeSn grown on GaAs showing the formation of etch pits. c) EDX characterization which confirms the formation of the etch pits before the growth of the ternary layer.

In order to study the "cross contamination" problem among the III-V elements and the IV elements, Ge, SiGe and SiGeSn have been grown and characterized after several III-V runs. In similar way, III-V compounds have been grown and characterized after SiGeSn growth. It is worth mentioning that a preliminary study of the "cross contamination" was already reported considering the growth of a InGaP/InGaAs/SiGe/Ge TJ structure [18]. This study was limited to measure the contamination of IV elements in III-V after SiGe deposition. This work, therefore, extends and somehow completes the previous one.

The cross contamination was firstly measured by SIMS. After verifying that the SIMS data agreed with ECV data, this last characterization technique was used to assess the reduction of contamination in the optimized samples. The Sn, Si and Ge contamination measured in AlAs/GaAs Bragg test structure is reported in Fig.4 a). The ECV profile measured on a GaAs/GaAs sample grown after the Bragg (DBR) test structure is reported in Fig. 4b). Both runs have been performed at a growth temperature around 630 °C (type I growth condition).
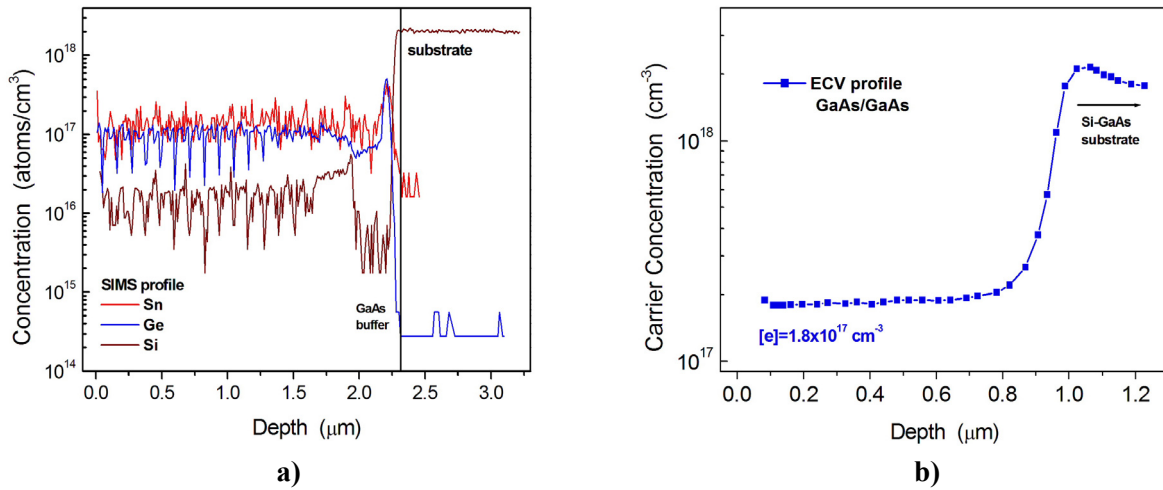
FIGURE 4. a) SIMS profiles of Sn, Ge and Si in the AlAs/GaAs DBR test structure grown after SiGeSn deposition and 8 μm of III-V compounds; b) ECV profile performed on a GaAs/GaAs sample grown after the AlAs/GaAs DBR test structure.

In spite of the low concentration in the alloy, Sn is incorporated like Ge to a level of $1\text{-}2*10^{17}$ cm^{-3} in AlAs and GaAs. It is worth noting that this contamination is measured after SiGeSn growth and other 8 μm of III-V deposition. The contamination measured in the same Bragg test structure grown just after SiGeSn growth was more than double (around $5*10^{17}$ cm^{-3}), however, even after several III-V run, a background contamination around $2*10^{17}$ cm^{-3} is always measured in the growth chamber, as shown in Fig.4 b). The incorporation of Ga, As, P and In in SiGeSn is reported in Fig.5 a).
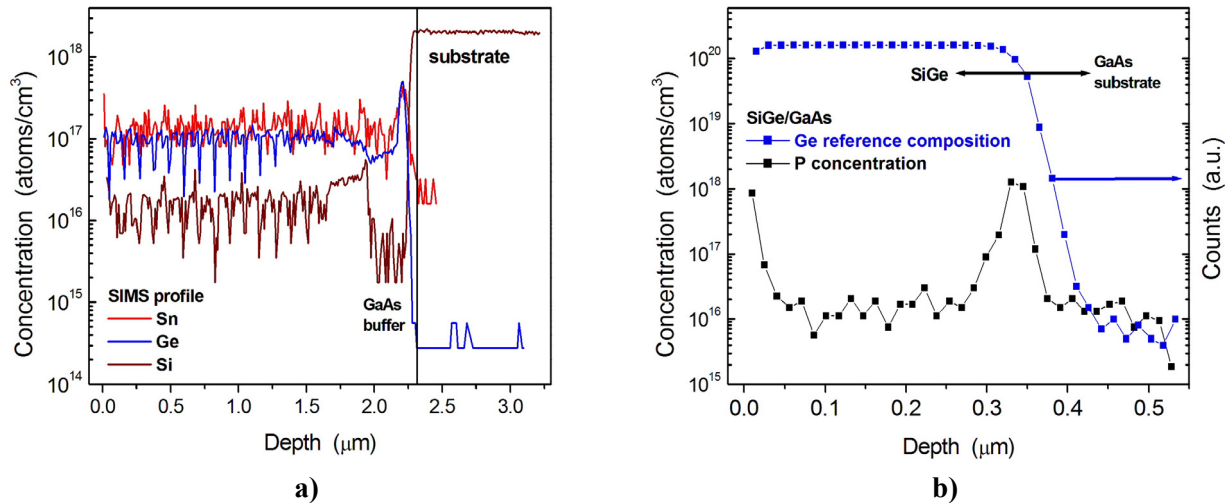

FIGURE 5. a) SIMS profiles of Ga, As, P and In in SiGeSn; b) SIMS profile of P in SiGe.

The very high contamination of As in SiGeSn is due to the fact that a small amount of AsH$_3$ is kept flowing during the growth of the ternary material, in order to improve the layer morphology. The anomalous behavior of P (whose concentration was found to increase during the run instead of remaining constant or decrease) was attributed to a possible contamination coming from SnCl$_4$ precursor. This hypothesis was checked by growing only SiGe. The result of the SIMS characterization of the SiGe test structure is reported in Fig.5b) and confirms the presence of P in the SnCl$_4$ precursors. In order to reduce the cross contamination in III-V compounds, the growth temperature was decreased to 500 °C (type II growth condition). For the growth of the IV-based elements several changes have been

considered: i) the elimination of arsine during the run, ii) a slightly decrease in the growth temperature and iii) a consistent increase of the growth rate from 1 nm/min up to 100 nm/min for Ge and from 0.1 nm/min up to 7 nm/min for SiGeSn. The reductions in the cross contamination obtained with the improved growth condition are reported in Fig 6. In Fig.6 a) InGaAs is grown starting with type I growth condition, the run is stopped and the InGaAs growth is carried out under type II growth condition. In Fig.6 b) InGaP is grown adopting type II growth condition, while the InGaAs buffer is grown under type I growth condition. The contamination is much more reduced if a GaAs substrate is used instead of Ge substrate. In Fig 6 c) the drastic reduction of the contamination in Ge is shown owing to the improved growth condition and the utilization of sufficiently thick layers.
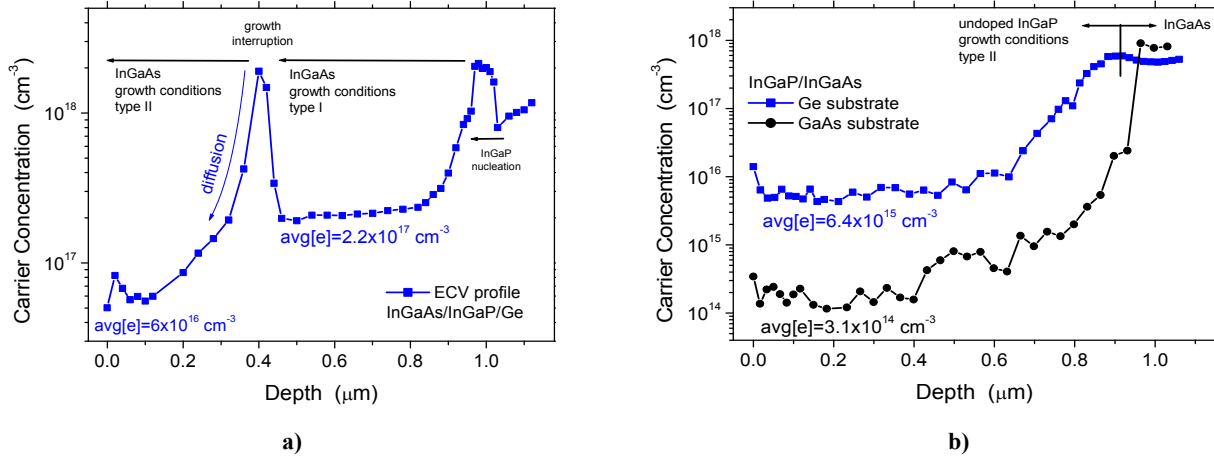
FIGURE 6. a) ECV profile of the IV elements in InGaAs grown with the growth condition type I and the improved ones, type II; b) ECV profile of the IV elements in InGaP which is grown with growth condition type II, considering different substrates.
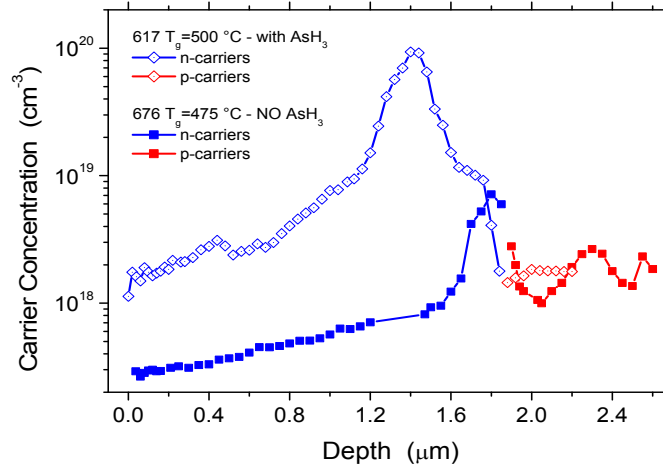
FIGURE 7. ECV profile of the III-V elements in Ge, considering different growth condition.

As expected, the reduction of the temperature and the increase of the growth are the key factors to reduce the contamination in the grown layers, since the former mainly reduces the evaporation of the impurities from the susceptor area, the later increases the dilution of the impurities. For the growth of IV based elements, the elimination of the arsine during the run plays a fundamental role in reducing the As contamination. Reducing the temperature has also the benefit of "freezing" the dopant diffusion and preserve the tunnel diode doping profile.

CONLUSIONS

SiGe(Sn) and III-V compounds have been deposited for the first time in the same MOVPE growth chamber with the purpose of preserving the competitive advantage of the monolithic approach in manufacturing 4-junction solar cells. SiGe(Sn) has been deposited both on GaAs and Ge substrates. A critical aspect related to the SiGeSn deposition on GaAs substrate has been evidenced when Cl-based precursors are selected. In particular, in order to avoid the formation of etch pits, likely due to the HCl etching action, a suitable intermediate layer is proposed to be deposited between SiGeSn and the GaAs substrate. It has been shown that, by a proper modification of the MOVPE reactor and by selecting proper growth condition, the contamination III-V elements in IV based materials can be drastically reduced from 10^{20} cm^{-3} to $2*10^{17}$ cm^{-3}, while the contamination of IV elements in III-V compounds can be reduced from $4\text{-}5*10^{17}$ cm^{-3} to $6*10^{16}$–$3*10^{14}$ cm^{-3} depending on the substrate used,. This contribution constitutes an important step ahead towards a fully MOVPE grown monolithic 4-junction InGaP/InGaAs/SiGeSn/Ge solar cell.

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