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# DEVELOPMENT OF MONOLITHICALLY INTEGRATED (Al)GaAs ON SILICON FOR TANDEM SOLAR CELLS

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**ABSTRACT:** We present here an innovative solution to heterogeneously integrated III-V materials on silicon based on the growth of micrometric GaAs crystals on silicon without any structural defects nor stress, using Epitaxial Lateral Overgrowth on Tunnel Oxide from nanoseeds (ELTON). This epitaxial method has the advantage of being compatible with cost effective processes, while using innovative growth mechanisms with very low III-V material requirement (a micron or so deposited and no III-V or Ge substrate required) helping keep costs competitive and with low use of critical raw materials. The main focus of this work is to address the issue of the doping determination of micrometric size GaAs crystals which is a pre-requisite for developing design and technology of multijunction solar cells based on an array of GaAs crystals free of structural defects. In a previous work, local electrical characterizations by  $\mu$ -PL have revealed a rather high non intentional p- type doping. Several growth solutions (effect of V/III ratio and use of alternative precursor) will be presented to lower these high non intentional p- type doping.

**Keywords:** Epitaxy, III-V Semiconductors, Silicon, Multijunction Solar Cell

## 1 INTRODUCTION

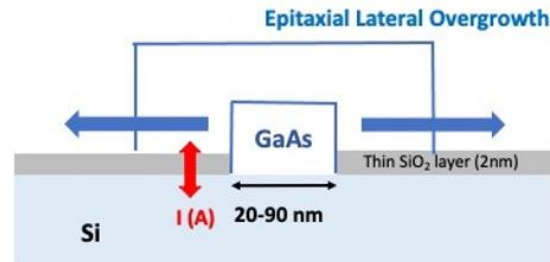
The monolithic integration on silicon of GaAs, and more generally of III-V semiconductors, would be a very promising route for the production of high efficiencies multijunctions devices in the manner of those developed for spatial applications on germanium, but at a much lower cost suitable for terrestrial PV applications. The lattice parameter mismatch leading to threading dislocations is however the major problem that many approaches have tried to resolve but to date no one has succeeded in achieving defect-free and cost-effective direct integration of the simplest GaAs binary III-V compound, on silicon.

In previous work, we have demonstrated the perfect integration on silicon of micrometric size GaAs crystals without any structural defects nor stress, using Epitaxial Lateral Overgrowth on Tunnel Oxide from nanoseeds (ELTON). This technic also leads to a very good electrical connection not only between the GaAs microcrystals and the Si substrate, but also across the GaAs/thin SiO<sub>2</sub>/Si sandwich (by tunnelling assisted transport) surrounding the nanoholes [1]. The principle of the ELTON technic is illustrated in Figure 1.

We aim now to extend this strategy to Al<sub>x</sub>Ga<sub>1-x</sub>As compounds, more specifically up to an Al content x=18%, which is the composition required to achieve current matching and an optimum conversion efficiency for an AlGaAs/Si tandem photovoltaic solar cell of 32% (derived from our realistic software model called SOL). The assessment of our SOL software has been fully proven by accurate modelling of the published experimental data of record multijunctions solar cells [2]. Nevertheless, before investigating AlGaAs alloy we will focus on the control of the residual doping of the simply binary GaAs compound.

The residual doping control in a single GaAs microcrystal is a pre-requisite to developing the future design and technology of multijunction solar cells based on this approach. Local electrical I/V measurements of the GaAs/Si heterojunction performed with CP-AFM showed a high rectification ratio but a high p-type non intentional doping level was suspected and related to high non-intentional carbon incorporation induced by trimethylgallium (TMGa) used as Ga precursor. The

precise doping level determination in a single  $\mu$ -crystal by local I/V or C/V measurements is difficult because in the first case the estimation is too indirect and in the later one, the capacitance values are too small to be easily measured. To obtain a better estimation of the doping level, we have developed a contactless method based on the measurement of the evolution of the bandgap versus temperature [3]. The bandgap value is extracted from the micro-photoluminescence spectra of a single GaAs crystal. The bandgap narrowing due to p-type doping is taken into account and the doping density can then be estimated from the fit of the bandgap evolution with temperature.



**Figure 1:** Schematic view of Epitaxial Lateral overgrowth on Tunnel Oxide from nanoseeds (ELTON): the growth only begins inside the nanoholes performed in the thin silica layer covering the silicon wafer and then extend laterally on top of the SiO<sub>2</sub> layer. The (tunnelling assisted) electrical connection between GaAs and the Si substrate through thin SiO<sub>2</sub> layer is indicated with the red bidirectional arrow.

This high carbon doping has been observed in the literature, and the concentration can be adjusted by increasing the V/III ratio during epitaxy [4]. Nevertheless, recent results obtained in our growth reactor not clearly seem to allow such a good control of the p-type doping level but this point will be further investigated with both higher growth temperatures and V/III ratio. However, a fallback solution is to adjust the p-type concentration by the use of TEGa (TriethylGallium) and TMGa together with TBAs. The use of TEGa with TBAs makes it possible to obtain low carbon concentrations of the order of 10<sup>15</sup>-10<sup>16</sup>cm<sup>-3</sup> reproducibly. The simultaneous use of TEGa /

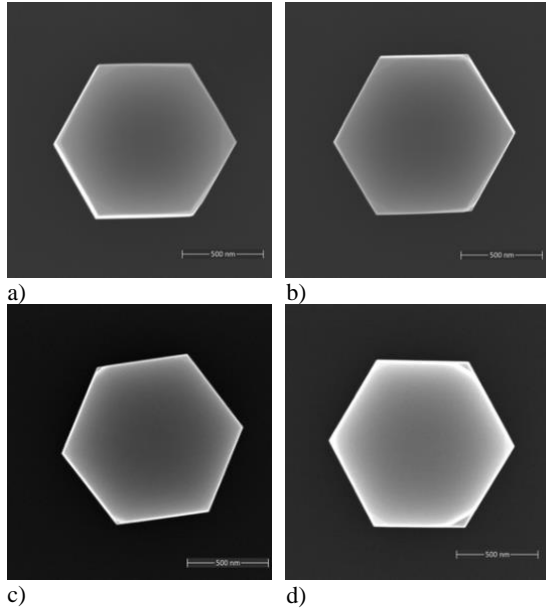
TMGa ratio in variable proportions is therefore expected to allow a good control of the level of doping over a range from  $10^{14} \text{ cm}^{-3}$  to  $10^{20} \text{ cm}^{-3}$ [5]. These routes to a better control of the non-intentional carbon incorporation and the further p-type intentional doping will be addressed.

## 2 RESULTS AND DISCUSSION

### 2.1 Micro-scale GaAs crystals growth

The GaAs  $\mu$ -crystal growth was carried out in a chemical beam epitaxy (CBE) system with the Epitaxial Lateral overgrowth on Tunnel Oxide from nano-seed (ELTON) technique. TriMethylGallium (TMGa), TriEthylGallium (TEGa) and TertiaryButylArsine (TBAs) were used as gas sources. The (111)Si wafers were cleaned using the modified Shiraki chemical cleaning which results in a reproducible ultrathin  $\text{SiO}_2$  layer with a thickness of 1.2 nm thick oxide layer as deduced from Auger electron spectrometry and HRTEM. The important next step is the opening of the nanoscale holes through the ultrathin silica layer prior to GaAs epitaxy.

To demonstrate the ability of the ELTON growth for the perfect integration of micrometric size GaAs crystals, we first used a random patterning of the silica layer directly performed in situ in the growth reactor. For this purpose, the nucleation seeds must be created. Therefore, in order to open nanoscale holes through the thin silica layer, the oxidized silicon substrate was fast ramped up  $750^\circ\text{C}$ , under vacuum, and maintain at such temperature during 1 min 30 s. This results in pure Si nano-areas formed via the reduction of  $\text{SiO}_2$  into volatile  $\text{SiO}$ .



**Figure 2:** Top SEM images of  $\mu$ -scale GaAs crystal sgrown on silicon using the ELTON Process for different V/III ratio with TBAs and TEGa as gas precursors. a)  $R = 6$ , b)  $R = 10$ , c)  $R = 18$  and d)  $R = 22$ .

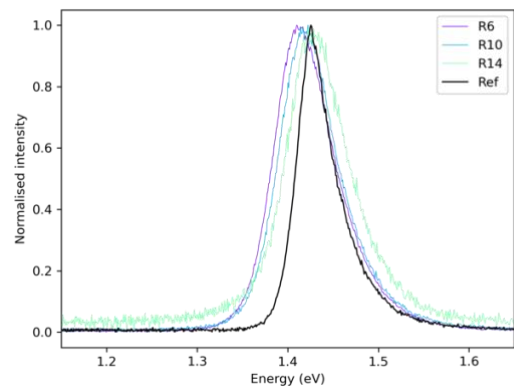
This method has the advantage of easily providing nanoscale seeds around 50 nm in width, randomly spaced at the surface of the oxidized Si substrate [1]. After this step, the GaAs epitaxy was initiated with a two steps procedure. The first step consists in introducing solely TBAs (during 2 min) at  $430^\circ\text{C}$ . In the second step TMGa, respectively TEGa, were also introduced while the growth temperature was increased up to  $575^\circ\text{C}$ . After, this

nucleation step that took 2 min, GaAs epitaxial lateral overgrowth was then continued for 45 min. In this paper we investigate particularly the effect of the As/Ga (V/III) ratio on the doping of GaAs  $\mu$ -crystals. For this purpose, several V/III ratios, denoted  $R$ , will be investigated. Such as 6, 10 and 14 for [TBAs]/[TMGa]. And 6, 10, 14, 18 and 22 for [TBAs]/[TEGa]. For the sake of clarity, the V/III ratios studied in this paper are not the same for TMGa and TEGa. In fact, the results given for TMGa correspond to a previous study in which we limited ourselves to  $R=14$ . Top SEM views of  $\mu$ -scale GaAs crystals grown on silicon using the ELTON Process for different V/III ratios with TBAs and TEGa as gas precursors are showed in Figure 2.

### 2.2 Micro-Photoluminescence (PL) experiments

$\mu$ -PL measurements were performed on a WITec alpha-300R confocal microscope in a backscattering configuration. Samples were under vacuum at  $10^{-3}$  mbar in a Linkam cryostat and probed at a requested temperature imposed by the temperature controller from 80K to 340 K, each 20 K. Samples were excited at 532nm through an Olympus 20x long working distance objective, with  $9\mu\text{W}$  laser power ( $360\text{nW}/\mu\text{m}^2$ ). Light is collected through a  $200\mu\text{m}$  pinhole, and resolved with a 150 grooves/mm grating, with 750nm blaze wavelength. The detector is an Andor TEC cooled CCD bar at  $-70^\circ\text{C}$ . For each spectrum, the camera thermal signal is removed.

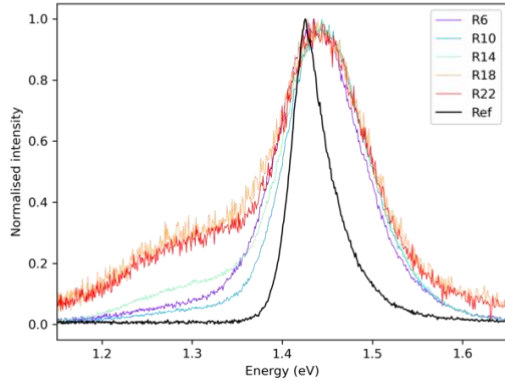
Figures 3 and 4 show PL spectra obtained at 300 K on GaAs/Si crystals made with the TMGa or TEGa precursor respectively, for the different  $R$  values indicated in the insert. The spectrum of an undoped GaAs wafer is also shown as a reference on each of the figures. We note that in the case of TMGa (Fig. 3), the PL peaks of the crystals have an energy position lower than or very close to that of the reference peak, whereas in the case of TEGa, the energy positions of the PL peaks of the crystals have an energy position higher than that of the reference. Figure 5 summarizes these trends by showing the evolution with  $R$  of the energetic position of these peaks as a function of the ratio  $R$ .



**Figure 3:** PL spectra at 300 K of GaAs/Si crystals made with the TMGa precursor for the different  $R$  values indicated in the insert. The black line (Ref) is the spectrum of an undoped GaAs wafer.

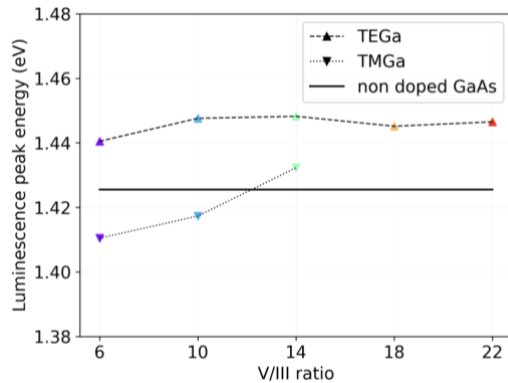
In the case of GaAs, it has been shown that the energetic position of the main PL peak is practically equal to the direct gap [6], to within a few meV (around 4 meV at 300 K). In Figure 5, peak energies below the reference value may therefore reflect an apparent reduction in the gap due to Band Gap Narrowing in the case of a P-type,

whereas peak energies above the reference value could be explained by the Moss-Burstein effect for a degenerate N-type material. If this interpretation is correct, the different behavior of TMGa and TEGa precursors may be related to the amphoteric character of carbon with respect to GaAs doping, given the different dissociation properties of the methyl and ethyl radicals present in these precursors.



**Figure 4 :** PL spectra at 300 K of GaAs/Si crystals made with the TEGa precursor for the different R values indicated in the insert. The black line (Ref) is the spectrum of an undoped GaAs wafer.

Figure 5 also shows that it appears difficult to finely control doping in GaAs by using only one or other of the precursors when growing with the CBE technique. The use of a mixture of the two precursors should, in principle, provide a better answer to this problem, but this route is likely to be more tricky to implement since, with TBAs, it will require the use of three precursor gases. However, before exploring this avenue, it will be necessary to analyse in more detail our interpretation of the evolution with R of the main peak shown in Figure 5.



**Figure 5 :** Evolution with R of the energetic position of the main peak of the spectra presented in Fig. 3 and 4 as a function of the ratio R. The upper (lower) curve is for GaAs/Si crystals made with the TEGa precursor (TMGa precursor) respectively.

To this end, we will exploit photoluminescence spectra measured at different temperatures in the range 100 K to 340 K. In particular, we will analyze the evolution of the characteristics of the main peak and the secondary peak which is clearly visible at 300 K in the case of TMGa in Figure 5. We only point out here that, in a certain range of lower temperatures, this peak becomes stronger and also becomes apparent in the case of TMGa. The detailed

interpretation of the evolution of the characteristics of these peaks with temperature will be one of the follow-ups to this work.

### 3 CONCLUSIONS

We have presented an innovative growth strategy based on Epitaxial Lateral Overgrowth On Tunnel oxide (ELTON) in order to monolithically integrate defect-free micrometric size (Al)GaAs crystals on silicon. Integrating these crystals in a regular array to have a quasi-complete covering of the Si substrate, without coalescence of the GaAs microcrystals, is therefore a very promising route to produce in a first instance an AlGaAs/Si tandem cell at an affordable cost for terrestrial PV applications.

A fine control of the residual doping with only TMGa or TEGa as the Ga precursors during the CBE growth could not be achieved in the present work. However we have shown that mixing TMGa and TEGa precursors could be a possible route to solve this problem, taking into account the amphoteric nature of the carbon with respect to GaAs doping, and the different dissociation properties of the methyl and ethyl radicals present in these precursors.

The results already achieved have permitted the identification of the bottlenecks and discuss the possible routes for III-V on silicon multijunctions solar cells as the tandem structure presented in this paper can be the building block for further extension to triple junctions.

### 4 ACKNOLEGMENTS

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