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Elaboration of III-V top cell for tandem cell with Silicon

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***Abstract* — We study GaInP alloy grown by molecular beam epitaxy (MBE) for single junctions solar cells. Growth was optimized to obtain a photo-conversion efficiency of 9.66%, without anti-reflection coating. Further characterization allowed the investigation of the remaining issues in the structures. Beryllium doped GaInP base layer was identified as the layer limiting the photo-conversion performance of the solar cells.**

***Index Terms* — III/V semiconductor, Silicon, tandem solar cells, GaInP, MBE.**

I. Introduction

Much research effort is currently dedicated to overcome the Shockley-Queisser limit. One of the main lead is III-V/Silicon tandem cell. In a two terminal tandem design with a Si bottom cell, ideal top cell has a 1.73 eV bandgap and allows to reach a 41.9% theoretical efficiency [1]. By adjusting their composition, $Ga_xIn_{1-x}P$ and $Al_yGa_{1-y}As$ alloys approach this optimal bandgap, they are good candidates and can be grown on GaAs substrate.

$Al_yGa_{1-y}As$ has a 1.73 eV bandgap with y=0.25, but it suffers from significant oxygen incorporation during the growth causing deep levels acting as recombination centers in the device[2] . Thanks to its lower sensitivity to oxygen, better efficiencies are currently obtained with $Ga_xIn_{1-x}P$ based solar cells grown with metalorganic chemical vapor deposition (MOCVD). Indeed single junction GaInP cell reached an efficiency of 20.8 % [3], Essig et al assembled a four terminals GaInP/Si tandem showing an efficiency of 32.45% [4], a photoconversion of 33.3% was reached using wafer bonding with a triple junctions GaInP/GaAs//Si tandem cell [5].

However, when lattice matched to GaAs substrates, $Ga_{0.51}In_{0.49}P$ properties vary with the growth conditions. Bandgaps from 1.83 to 2 eV were reported at this composition [6]. Moreover, atomic ordering [6] is often observed in this alloy, inducing carrier lifetime variation [7] and carriers diffusion anisotropy [8].

Here we focus on the impact of MBE growth conditions on GaInP properties and report their effect on GaInP cells. We then identify the main drawbacks related to Be-doping and P solid source used for the growth of phosphide alloys.

II. Experimental results

III-V semiconductors samples were grown by a Riber Compact 21 MBE. Beryllium and Silicon, serve as p, and n-dopant, respectively. GaInP characterization layers and single junction solar cells were grown on (100) GaAs substrate.

Solar cells comprise a 1 µm p-GaInP absorber, an AlInP window, a 50 nm n- GaInP emitter, AlGaInP back surface field and GaAs contacts layer (Fig. 1), they are processed via wet etching. Ni/Ge/Au, and Ti/Au, metallic contacts allow the formation of ohmic contacts with the cell. Various characterizations on AlInP passivated p-doped GaInP enabled the material optimization for photovoltaic application.

Cells are characterized under AMG 1.5 illumination from an Oriel solar simulator, external quantum efficiency (EQE) is measured with a monochromator using a Si reference cell.

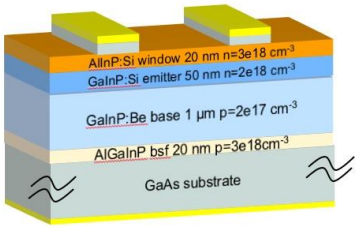

Fig. 1. Optimal GaInP solar cell structure in this study

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A. Study of GaInP growth

As said earlier growth conditions have significant impact on phosphides properties. Here we study the influence of the growth temperature Tg and the V/III ratio on GaInP. The goal is to maximize the PL efficiency of the GaInP, as it is a sign of better material quality and promotes photon recycling in the cells. The growth rate was maintained at 1µm/h for all samples, V/III ratio was varied by modifying the value of the beam equivalent pressure of phosphorus BEP(P). Two series of sample were grown, first a batch at a fixed V/III ratio of 12 and growth temperatures from 450°C to 580 °C. Then a batch with fixed growth temperature of 500°C and a V/III ratio varied between 12, 7.3 and 4.5.

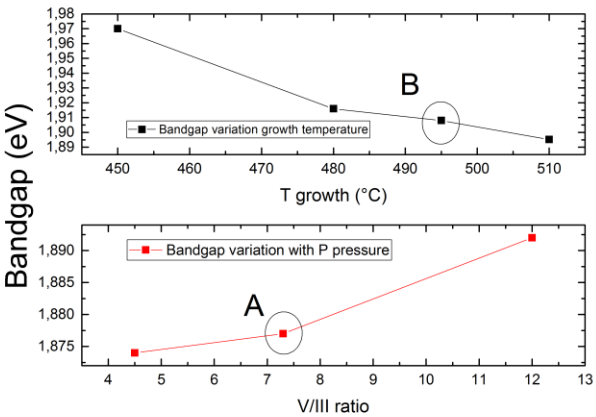

Fig. 2. Bandgap measured with photoluminescence characterization at 10 K of a batch with: fixed V/III ratio and growth temperature variation (in black), Phosphorus BEP variations and fixed growth temperature (in red), measured with photoluminescence at 10 K.

Samples grown at 540 and 560 °C were of poor quality. In fact, at these temperatures, In and P desorption damage the growth front and causes increasing roughness of the material.

Optical bandgap was measured at low temperature with photoluminescence at 10 K. Black squares (top x-axis) Fig. 2, displays the results for the influence of the temperature. Increasing the temperature from 450°C to 510°C (at a 12 V/III ratio) causes a reduction of the optical gap from 1.97 eV to 1.89 eV equivalent to a difference of 80 meV. The composition of the sample was checked by means of X-ray diffraction, only 13 meV is expected to result from the average composition variations of the samples grown between 450°C and 510°C.

Decreasing the V/III ratio from 12 to 4.5 (at a temperature of 500°C) results in a reduction of the optical bandgap too, 1.87 eV was observed at the lowest V/III ratio (red squares and bottom x-axis).

Scanning Transmission Electrons Microscopy (STEM) was performed on the sample grown at a 7.3 V/III ratio (sample A Fig. 2). STEM images exhibit contrast variations perpendicular to the growth axis, they result from composition modulation in the alloys. Present in both the AlGaInP and GaInP layer they arise from periodic changes of the In content in the alloy. At higher V/III ratio, no composition modulations were detected in the samples. Thus bandgap below 1.88 eV results from spontaneous lateral composition modulations (LCM). Bandgap fluctuation observed with the growth temperature changes cannot be attributed to such important LCM effects as sample grown in condition B (Fig. 2) appears homogenous. However we assume that lighter composition modulation in the GaInP causes the bandgap reduction observed.

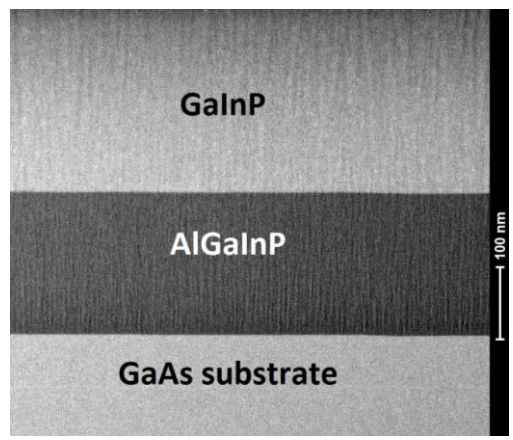

Fig. 3. STEM image of sample labeled "A" (Fig. 2), Lateral composition modulation seen in the phosphide layers.

In addition to composition fluctuations, the decrease of the V/III ratio reduces the PL intensity of the sample. Although LCM can improve carriers lifetime [7], we presume from the low PL intensity of sample A that this weak lateral composition modulation is not sufficient to benefit from carriers localization effects. It was thus chosen to keep the V/III ratio to 12 for the growth of cells.

PL spectra for the batch studying effects of growth temperature are shown Fig 4. Best PL intensity occurs at Tg=495°C. Sample grown at 450°C, which has highest bandgap, have the lowest PL efficiency compared to the other samples. The evolution of the PL of the samples with temperature was studied. Sample grown at 495°C exhibits Varshni type behavior with small unhooking to the Varshni law at low temperatures, this is often observed for phosphides presenting few localized states [9]. Sample grown at 450°C presents two peaks. A high energy peak with the behavior as previously described, a second peak which is only visible at low temperature and whom position exhibits an inverted S-shape.

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This inverted S-shape is characteristic of an important localized states concentration [10], [11], it evidences a concentration of localized state more important than in other samples. Moreover the low PL intensity of this sample lead to the assumption that it suffers from more non-radiative defects too. Therefore the optimal growth temperature for GaInP is from 495-500 °C

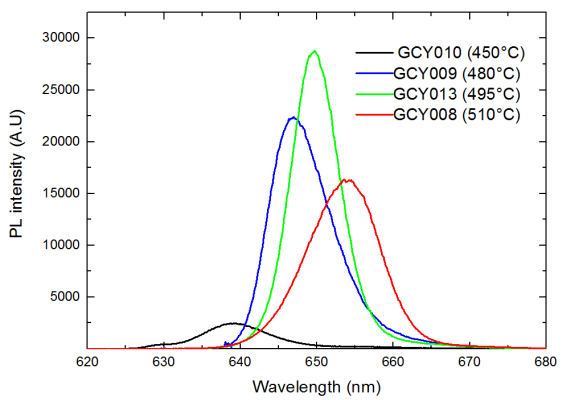

Fig. 4. PL spectra of GaInP grown at different temperatures, measured at 10 K.

B. GaInP solar cell

The effect of growth temperatures was tested on GaInP solar cells, two identical cells were grown at 450°C and 500°C. Table I details the performance gap between these cells, when grown at 450°C the cells have a 4.9 % photoconversion efficiency with a fill factor of 0.68, a Voc of 1.1 V and a short circuit current of 6.22 mA.cm^{-2} . When the cells are grown at 500 °C the cells exhibit much better characteristics, a 8.15 mA.cm^{-2} Jsc, an open circuit voltage of 1.23 V and FF of 0.78 resulting in a 7.87% efficiency.

These results confirm that growth temperatures around 500°C allow to grow GaInP cells of better quality.

Work on the optimization of the structure of the GaInP single junction (not detailed here) led to further improvement of the efficiency to 9.66% without anti-reflection coating. The structure of the cell is displayed Figure 1.

TABLE I
IV CHARACTERISTICS OF GAINP CELL AT 1-SUN. EFFECT OF GROWTH TEMPERATURE ON GAINP CELL

Tg(°C)	Jsc (mA.cm^{-2})	Voc (V)	FF	Efficiency (%)
450°C	6.22	1.1	0.68	4.9
500°C	8.15	1.23	0.78	7.87

During the studies led for structure optimization the base was identified as the limiting factor for the cells. In order to illustrate this diagnosis, the base thickness was varied and cells with 1 µm, 750 nm and 500 nm base were compared.

TABLE II
IV CHARACTERISTICS OF GAINP CELL AT 1-SUN. EFFECT OF THE BASE THICKNESS

Base thickness (nm)	Jsc (mA.cm^{-2})	Voc (V)	FF	Woc(V)	Efficiency (%)
1000	9.05	1.3	0.821	0.639	9.66
750	8.74	1.266	0.807	0.633	8.93
500	8.91	1.269	0.823	0.626	9.31

Reducing the base thickness should result in a decrease of absorption and therefore a drop of both Jsc and efficiency. As detailed in Table II, the reduction of the base thickness has negligible effect on overall efficiency and only 4% photocurrent reduction occurred when halving the base thickness.

This indicates a bad base quality, where the recombination of the generated carriers limits the photocurrent collection. Indeed, the generated carriers diffusion length is believed to be so low that photons absorbed above a 500 nm base thickness limit do not contribute to the photocurrent.

The Woc is a parameter often used to assess the quality of solar cells. It is defined as the difference between the bandgap of the cell and its Voc [12]. The lower is Woc the better is the cell quality and value as low as 0.4 V are reported for performant cells. It is expressed as follows:

$$Woc = \frac{Eg}{q} - Voc$$

Where q and Eg are elemental charge and bandgap energy, respectively.

The bandgap of the cell was estimated from the composition measured with X-ray diffraction. Table II also reports the Woc of the cells, one first notices Woc values above 0.6 V for all the cells, confirming a non-optimal quality of grown materials. It is noteworthy that a 13 mV Woc decrease occurs at the lowest the base thicknesses, confirming that poor base quality limits the cell.

Final illustration to this limitation, Figure 5 gathers the EQE of the three cells of this study. They exhibit only little differences in the long wavelength range characteristic of the base response. Moreover comparing the EQE shape of the GaInP

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cells with the shape of the EQE of an AlGaAs cell we notice a more constant response with AlGaAs in the long wavelength range and the EQE displays a steep drop around 710 nm. On its side GaInP cells have a slow EQE decrease starting from 500 nm. It is clear that this results from better p-AlGaAs compared to p-GaInP.

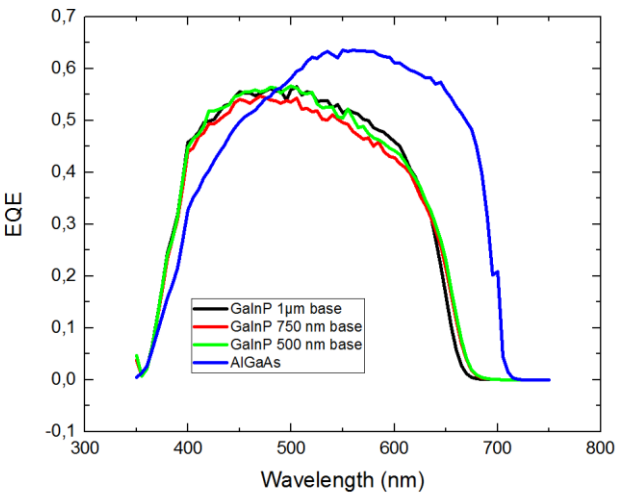

Fig. 5. EQE for GaInP cell with different base thicknesses. Comparison with 1-µm-thick AlGaAs cell.

B. Investigation on the p-GaInP limitations

Fitting our cells response, the carriers generation and recombination profile with depth were simulated. In the base, beside the first 200 nm from the p-n junction, generation and recombination rates are equal. It means that in most of the base, the collection probability of photogenerated carriers is low since most of them recombine before reaching the p-n junction.

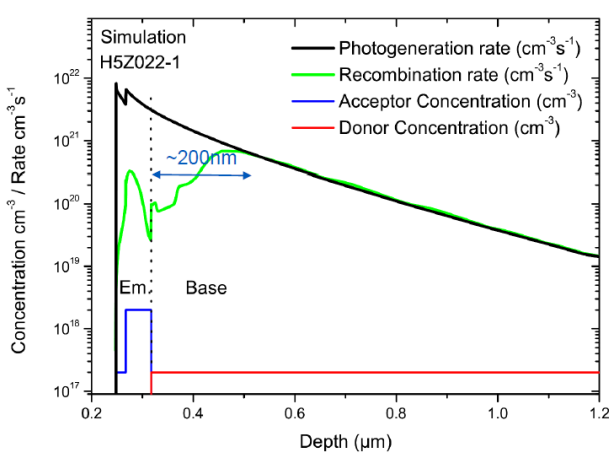

Fig. 6. Generation and recombination rates profile with depth, obtained from fitting experimental data of GaInP cell.

Time resolved fluorescence imaging (TR-FLIM) [13][14] was performed on AlInP passivated GaInP grown in the same conditions as the base layer of the cell. Using this method, we observed time-resolved PL profiles following a pulsed local illumination. Fitting the acquired transients to the continuity equation allowed to determine the lifetime and mobility in our base layer material. Despite a carrier lifetime of 2.3 ns, we determine a diffusion length of 258 nm resulting from a low carrier mobility.

III. Discussion

Despite GaInP optimization via adjustment of the growth it seems that material issues are still sources of limitations in GaInP single junction cell. Indeed several observations implicate the Be-doped GaInP as the factor limiting the conversion efficiency: between 500 and 1000 nm, the base thickness has little impact on the photocurrent and the drop of the EQE in long wavelengths is characteristic of a poor collection of carriers generated in the base.

Studying the transport properties of the generated carriers in the p-GaInP, both cell modeling and luminescence results indicate diffusion length bellow 300 nm for minority carriers. It seems that this limit originates from low mobility in the GaInP alloy. We suspect that the P solid source induces the incorporation of n impurities (in particular Si and S) in the p-doped layers [15], indeed a n-type non intentional doping of 1.10^{16} cm^{-3} is measured in the GaInP grown. This non intentional doping needs to be compensated in order to obtain p-doped alloy and we are therefore limited to a minimum doping level of 2.10^{17} cm^{-3} in the base. Both majority and minority carriers mobility decrease with the doping level [8], [16]. Fig. 7 illustrates doping level effect on majority carrier mobility measured with Hall Effect. In black, the AlGaAs with lower doping levels accessible as phosphorus is not used during its growth.

Moreover for identical p doping levels carrier mobility is higher in AlGaAs than in GaInP (in red). Therefore we expect better carriers transport in p-doped AlGaAs, resulting in better collection of carrier generated in the base of AlGaAs cell (Fig. 5).

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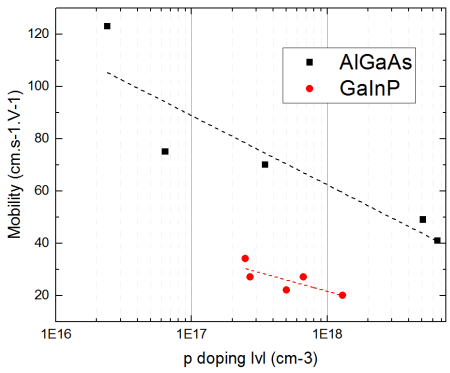

Fig. 7. Majority carrier mobility for p-doped GaInP and AlGaAs grown by MBE. Measured with Hall effect.

IV. Conclusion

We report on impact of growth conditions in GaInP single junction solar cell performances. At a 1 µm/h growth rate best conditions were found to be 500 °C and a 12 V/III ratio. 9.66% efficiency was obtained without anti-reflection coating. We identified p-doped GaInP as the limiting layer of the structure. Other studies comprising cell modeling and TR-FLIM led to the conclusion that small diffusion length in the solar cell prevents it from improving the photocurrent. In further work described elsewhere we explain how this limitation could be overcome structure design engineering and the use of a heterojunction.

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