Degradation of subcells and tunnel junctions during growth of GaInP/Ga(In)As/GaNAsSb/Ge 4-junction solar cells

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Abstract

A GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell grown using the combined MOVPE+MBE method is presented. This structure is used as a test bench to assess the effects caused by the integration of subcells and tunnel junctions into the full 4J structure. A significant degradation of the Ge bottom subcell emitter is observed during the growth of the GaNAsSb subcell, with a drop in the carrier collection efficiency at the high energy photon range that causes a ~15% lower $J_{sc}$ and a $V_{oc}$ drop of ~50 mV at 1-sun. The $V_{oc}$ of the GaNAsSb subcell is shown to drop by as much as ~140 mV at 1-sun. No degradation in performance is observed in the tunnel junctions, and no further degradation is neither observed for the Ge subcell during the growth of the GaInP/Ga(In)As subcells. The hindered efficiency potential in this lattice-matched 4J architecture due to the degradation of the Ge and GaNAsSb subcells is discussed.

Keywords: four-junction solar cell, dilute nitride, MOVPE, thermal load, degradation

1. Introduction

Multijunction solar cells based on dilute nitride subcells represent a promising route to achieving high conversion efficiencies using a monolithic design. This approach has already
shown high efficiencies in 3-junction (3J) solar cells grown by MBE [1], and combined MOVPE + MBE [2]. 4J solar cells grown on a Ge substrate, which acts also as the 4\textsuperscript{th} junction, are attractive for its growth simplicity: it conceptually consists on just adding the dilute nitride junction to the standard and mature GaInP/Ga(In)As/Ge 3J solar cell. A full MOVPE process is desirable, to minimize fabrication cost. However, obtaining high photovoltaic quality dilute-nitride subcells by MOVPE remains to be accomplished, as compared to the successful implementation of 3J by MBE [1]. A recent publication has shown positive steps towards achieving a 4J using a full MOVPE process [3], but the low quality of the dilute-nitride is still the main limitation.

At this stage of development, it is pertinent to have a closer look at the integration of components forming the 4J structure. For example, the insertion of the dilute nitride subcell in the 3J structure brings about added thermal loads to the Ge bottom subcell, an effect accentuated by the fact that dilute nitrides usually require an annealing step to improve their electronic properties. The dilute-nitride subcell itself suffers annealing during the growth of the upper subcells, which could be expected to have an impact on its performance. The focus has to be put in identifying and quantifying these effects, and redesigning the growth process to minimize their impact.

In this work we present a detailed characterization of our 4J solar cell, based on a prototype structure achieved by a combination of MOVPE + MBE growth methods, and using a GaNAsSb junction. This solar cell succeeds in integrating four component junctions into a monolithic, lattice matched structure, but it is still far from being a high efficiency device, mainly due to sub-optimum characteristics of the dilute nitride subcell. However, the device provides valuable insight into the integration of the dilute nitride subcell into a 4J solar cell. We focus mainly on the effect of thermal load on the performance of the Ge and GaNAsSb bottom subcells, and the tunnel junctions. It is found that significant losses are at stake, mainly in the Ge and GaNAsSb subcells, which can limit the potential of this 4J solar cell structure to compete in efficiency with other architectures.

2. MOVPE+MBE 4J SOLAR CELL

The objective 4J solar cell structure is depicted in Fig. 1 (left). As explained in the introduction, the novelty in this structure consists in integrating a 1eV GaNAsSb subcell in
the standard GaInP/GaAs/Ge triple-junction solar cell. For this, a combination of MOVPE and MBE processes are used. First, a GaInP nucleation layer is grown by MOVPE on the Ge substrate, optimized for a suitable transition from non-polar group-IV to III-V polar semiconductor and obtain a defect free surface for the growth of the subsequent III-V layers. Besides, a n-p junction is formed in the p-type doped Ge substrate by unintentional (but quantified) in-diffusion of phosphorous during the growth of the nucleation layer [4]. In the same run, the bottom tunnel junction is grown, and capped with a GaInAs layer. This structure is then transferred to an MBE reactor, where the GaNAsSb dilute nitride subcell structure shown in Fig. 1-right is grown. The MBE process includes an in-situ annealing of the dilute nitride structure grown (5 min at 700 °C), which is needed to improve the material quality. Abundant literature is available reporting the effects of annealing on dilute nitride materials and the mechanisms behind, see for example [5]–[9] for GaNAsSb and others. With this dilute-nitride solar cell structure we have achieved our best performance so far using GaNAsSb [10]. The absorber thickness used is just 1000 nm, which is lower than needed for a complete optical absorption. This thickness was used since it allowed to achieve the highest quantum efficiency: given the low carrier diffusion length in this material, thicker absorber layers did not give rise to higher quantum efficiencies [10], [11]. Finally, the sample is transferred back to the MOVPE reactor for growing the middle tunnel junction and the top GaInP/Ga(In)As tandem structure. The thicknesses of the absorber layers are 3500 nm and 900 nm for the Ga(In)As and GaInP subcells, respectively. All layers in the 4J structure are lattice-matched to the Ge substrate.
3. Experimental

The MOVPE processes were carried out in a horizontal, research-scale reactor model AIX200/4, using AsH\textsubscript{3}, PH\textsubscript{3}, TMGa, TMAI, TMIn, DETe, DMZn and DTBSi\textsubscript{2} as constituent and dopant precursors. The reactor is equipped with an in-situ reflectance (R) and reflectance anisotropy (RA) spectroscopy tool model LayTec 2000. The same tool also provides information about the true temperature of the wafer surface, based on pyrometer detection of the emission from the sample during growth. The GaNAsSb 1 eV junction structure, with a composition of N and Sb of 2.4% and 6.5% respectively [12], was grown using a MBE system, with solid evaporation sources for group III materials, such as gallium, indium and aluminum. Arsenic and antimony used in the growth were provided by valved cracker sources, at a temperature of 900 °C to crack the arsenic and antimony, respectively. Nitrogen atoms were provided using a radio frequency (RF) plasma-assisted nitrogen source, set at a power of 180W. The MBE system was also equipped with Reflection High-
Energy Electron Diffraction (RHEED) system for in-situ monitoring of the change of surface reconstruction during the growth. The lattice-matching of the structures grown was measured by High Resolution X-Ray Diffraction, using a Panalytical X’Pert Pro MRD tool. All the layers in the structures used for this work are lattice matched, with a separation between the peak of the Ge substrate and the layers below 200 arc seconds in the rocking curves taken for the 004 reflection.

The solar cells were processed by gold-based metallization using standard photolithographic techniques. Solar cell devices with an area of 0.1 cm$^2$ obtained using gold electroplating were used to determine the external quantum efficiency and 1-sun electrical characteristics. For the analysis of operation at high concentration, 0.01 cm$^2$ solar cells with a concentration front grid manufactured using the AuGe/Ni/Au alloy by metal evaporation and annealing (higher metal quality than electroplated Au) were used. This way, the series resistance due to the contacts could be minimized, ensuring it would not obscure the measurement of the electrical parameters of interest of the solar cell semiconductor structure up to high concentrations.

External quantum efficiency (EQE) measurements and spectral reflectivity (R) were taken using a custom-built system based on a 1000W Xe-lamp and a triple-grating monochromator, and equipped with monitor sensors to account for the light source instabilities. 4 LED sources were used for light biasing of the subcells. A voltage bias could be applied when necessary using the internal function of the SR570 transconductance preamplifier of the EQE system. The appropriate voltage for this purpose was determined using the method explained in [13]. Solar cell current-voltage (I-V) curves were taken using the four-point probe technique on a temperature-controlled chuck using a 4-quadrant source-monitor unit. Light-I-V measurements were obtained using a class A solar simulator based on a 1000W Xe-lamp. Additional 1-sun I-V curves with calibrated spectrum composition were measured using a setup available at the National Renewable Energy Laboratory (NREL - USA) based on a Xe-lamp and high power LEDs [14].

The QE and reflectivity modelling was carried out by computing the absorbance in each layer of the structure using the Generalized Matrix Method [15] for the experimental layer thicknesses obtained and using typical n and k data from the literature. Then the carrier collection in each layer was adjusted to fit the experimental QE.
4. Performance of the 4J solar cell

The performance of the 4J solar cell implemented was characterized. Firstly, the measured EQE and R of this solar cell, without anti-reflection coating (ARC), is shown in Fig. 2. The EQE and R was used to calculate the internal quantum efficiency (IQE) using \( \text{IQE}(\lambda) = \frac{\text{EQE}(\lambda)}{1-\text{R}(\lambda)} \), which is shown also in Fig. 2. The top GaInP and Ga(In)As subcells exhibit EQE and IQE similar to obtained when growing them in GaInP/Ga(In)As/Ge 3J solar cells developed in our lab [16]. The GaNAsSb subcell exhibits a low EQE due to the low material quality obtained combined with a thin absorber layer, as commented previously [10], [11]. The IQE values obtained for this subcell are around 0.6 and below. It is not straightforward to analyze the quality of the Ge bottom cell from its wavy EQE, but the IQE is smoother and shows clearly a low carrier collection efficiency which should be close to 1 in these solar cells, as will be shown later. The table on the right lists the short circuit current (\( J_{sc} \)) calculated using these EQE and IQE and the AM1.5D G173 solar spectrum. This makes explicit the limiting \( J_{sc} \) of the GaNAsSb, but also shows that the Ge bottom cell produces less photocurrent than the top GaInP and Ga(In)As subcells. This is the combined result of a low performance of the Ge subcell, caused by degradation during the growth of the upper layers in the structure, and of a non optimized splitting of the spectrum by the subcell bandgaps used. These two issues are discussed in the following sections.
Fig. 2. EQE and IQE of the 4J solar cell implemented for the cases listed in the legend, and table summarizing the short circuit current densities of each subcell calculated using the AM1.5D G173 solar spectrum.

The dashed lines in Fig. 2 show the modeled IQE of the GaNAsSb and Ge subcells assuming a carrier collection efficiency of 1 for both and an optically thick GaNAsSb. The $J_{sc}$ obtained using these modeled IQE show that even achieving an ideal carrier collection efficiency in the bottom subcells, they would still limit the current of the 4J. Note how making the GaNAsSb optically thick in the ideal case gives rise to an even lower $J_{sc}$ in the Ge bottom cell. This means that future optimizations of the 4J structure will require modifying the transparency of the top junctions to equilibrate the $J_{sc}$ in the subcells, either by lowering their thickness or, ideally, by tweaking their bandgap towards higher values. This illustrates the fact that achieving the full potential of this 4J based on Ge substrates and a dilute nitride subcell is not as simple as just inserting the dilute nitride subcell in the standard GaInP/Ga(In)As/Ge 3J structure.

Dark and 1-sun I-V curves were taken on the 4J devices too, and the results are shown in Fig. 3. The 1-sun result using unfiltered Xe-lamp shows a good shape in the I-V curve and a reasonable FF. However, this is so because under this spectrum the top cell is the limiting junction. Using spectrally adjusted AM1.5D-G173 spectrum by means of a calibrated solar simulator at NREL, as explained in [14] (see section 3), the I-V curve shows a very different result, underscoring the importance of using a well calibrated spectrum in order not to veil the actual influence of a junction on the performance of the whole multijunction solar cell. A
shunt-like behavior with a low FF can be seen. This behavior fits the previous simulation predictions obtained by including the measured electrical behavior of the GaNAsSb junction, as explained in [11]. This electrical behavior includes a field-assisted collection, which causes the photocurrent variation with voltage, similar to the effect of a shunt.

The \( J_{sc} \) of the 1-sun I-V curve corresponds to the photocurrent of the GaNAsSb junction obtained using the EQE measured (see Fig. 2), as expected. The \( V_{oc} \) measured is 2.44V. This \( V_{oc} \) is rather low, as compared to state-of-the-art GaInP/Ga(In)As/Ge 3J solar cells developed in our lab, which exhibit \( V_{oc} \) of around the same value [16]. This means that the \( V_{oc} \) increase expected with the insertion of the GaNAsSb subcell is not attained. The \( V_{oc} \) of the GaNAsSb as a single-junction device was shown to be around 420 mV [10], which means that this voltage is lost during the integration of the 4J components.

![Graph](image)

**Fig. 3.** 1-sun (left) and dark I-V (right) curves of the 4J solar cells developed. The 1-sun curves are taken using an unfiltered Xe-lamp source and a source spectrally adjusted to match the AM1.5D-G173 spectrum. The dark I-V curves are measured on two solar cell devices with different areas, and the dashed line is the fit to a 1-diode model with the ideality factor shown.

Concerning the dark-I-V curves, shown in Fig. 3-right, a shunting component can be observed for current densities up to around 150 mA/cm\(^2\) (which would correspond to ~25 suns in these solar cells). The cause of this can be attributed to the observable dispersed micro-defects on the sample surface due to imperfectly clean conditions during the MOVPE to MBE system transfer. Smaller area devices show a weaker shunting effect, as shown in Fig. 3, which can be explained as a lower number of these micro-defects falling...
in the device area (the dark I-V curves shown correspond to the best devices). Anyway, this shunting affects the $V_{oc}$ at 1-sun, and can account for a significant voltage loss. For higher current densities the shunt effect vanishes, so it does not affect the performance under concentrated light. The ideality factor can be measured to be 6 up to the current density where the I-V curve shape starts to be dominated by the series resistance (around 15 A/cm$^2$, which corresponds to about 1000 suns). This value corresponds roughly to the ideality factor of the GaNAsSb subcell, which was measured to be $\sim$2, added to the ideality factor of 3J developed previously at IES-UPM which was $\sim$4 [16]. An ideality factor of 1 in each subcell is desirable, which would give an ideality factor of 4 for the whole 4J structure. However, as long as the integration of components is concerned, the ideality factor of each subcell does not appear to be affected.

5. Degradation analysis

The shunt-like behavior caused by micro-defects explained in the previous section produces a significant voltage drop at 1-sun, but it is not intrinsic to these solar cells since it can be circumvented by proper reactor transfer procedures. Moreover, it does not appear to affect the performance of these solar cells under concentration. However, other integration effects inherent to these solar cell structures appear to be affecting the bottom subcells and must be assessed in order to elucidate additional voltage loss sources, and to evaluate the degradation of solar cell performance parameters such as the EQE.

The main cause for degradation expected is the thermal loads applied to the subcells and tunnel junctions during the growth of the upper layers. In Table 1 we show a summary of the growth temperatures, growth times and total annealing times to which each main component of the 4J solar cell is subjected to in our MOVPE + MBE combined process. These values determine the thermal budgets in each case. In this work we focus on the parts that suffer the heavier thermal loads in the 4J structure: the Ge bottom subcell, bottom tunnel junction and GaNAsSb subcell.

The study of the degradation of the component subcells in these 4J devices is not straightforward. Firstly, the electroluminescence technique [17] cannot be used to ascertain the internal subcell voltages ($V_{oc}$) due to the undetectable emission of light from the dilute nitride subcell at room temperature. Despite the fact that good measurements could be
taken, as shown in Fig. 2, the EQE of the subcells is also troublesome to measure, due to
the Ge subcell breakdown voltage and shunt effects [13] and the voltage-dependent
response of the GaNAsSb subcell. Moreover, the complexity of the 4J structure complicates
the modeling and introduces uncertainties that can obscure the actual reasons for the
degradation of the subcells. Hence, the approach followed consists on accessing the bottom
Ge subcell in the 4J structure by etching the upper layers, while the degradation of the
GaNAsSb subcell was studied by applying an equivalent thermal load to nominally identical
single-junction devices grown separately.

A. Degradation of the Ge bottom subcell.

In our 4J growth process, the Ge bottom subcell is annealed during almost 5 hours at
temperatures ranging from 550 to 700 ºC, as can be seen in Table I. As compared to the 3J
case, the insertion of the dilute nitride subcell increases the thermal load to the Ge bottom
subcell and tunnel junction. Although the growth time for the dilute nitride subcell is long in
the MBE step, the temperature used is relatively low (460-600 ºC), as compared to typical
MOVPE temperatures used. On the other hand, an annealing step is used at the end of the
dilute nitride growth, at a higher temperature (700 ºC) but during a very short period of time.
With this, it is not obvious to predict the real impact of this added thermal load, and we
assessed it empirically by examining samples at different stages of the MOVPE + MBE +
MOVPE process. For this, we used the structures obtained at the end of the 1st MOVPE, the
MBE and the 2nd MOVPE steps. These structures correspond to the Ge subcell, the
Ge/GaNAsSb tandem and the full 4J structure, respectively (see Fig. 1). By etching the
upper layers in each of these structures we could access the Ge bottom cell and measure it
as a single-junction solar cell, as explained before.
A first test was to measure the carrier concentration profile in the Ge junction, which we did by taking electro-chemical capacitance-voltage (ECV) profiles of Ge junctions, shown in Fig. 4. The dopant diffusion at the emitter is evident: the average carrier concentration level and thickness of the emitter changes substantially during the growth of the 4J. Not less importantly, as will be shown later, a compensated region appears at the surface of the emitter, which does not change in thickness significantly during the growth of the top GaInP and Ga(In)As subcells. This region is caused by the in-diffusion of III-elements from the GaInP nucleation layer, and can be expected to act as a sink for minority carriers, causing a high interface recombination.

EQE and specular reflectivity were measured on these solar cells, and then the IQE was calculated. The results are shown in Fig. 5. Firstly, these measurements reveal an important degradation of the carrier collection efficiency in the higher energy region. The EQE of the degraded Ge junction is accurately modeled including the compensated layer (~40 nm) with 0 collection efficiency and a lower collection efficiency in the emitter bulk (~70%). An additional point to note is the fact that the QE degradation happens mostly during the growth of the GaNAsSb subcell, and the QE remains virtually the same after growing the top GaInP/Ga(In)As tandem. This is probably related to the fact that the compensated region width does not change significantly between the 2J and 4J case, as shown in Fig. 4. The
changes in the emitter carrier concentration profile when growing the top GaInP/Ga(In)As subcells observed in Fig. 4 do not appear to produce a modification in its bulk carrier collection properties.

Fig. 5. EQE of the Ge subcell as: single junction (blue), in a GaNAsSb/Ge 2J (red), and in the 4J (green). The reflectance measured was virtually identical for all cases, so only one curve is shown for clarity. The continuous lines are fits to the EQE and reflectance. The dashed lines correspond to the IQE calculated using the fitting curves.

It is important to point out that the apparent severity of the IQE degradation shown in Fig. 5 is lessened by realizing that the Ge subcell absorption range, when working as a subcell in the 4J structure, falls in the lower photon energy region, as indicated in Fig. 5, where the degradation is not so severe. Still, the IQE drop in that region produces a \( J_{sc} \) drop of ~15% as calculated for the AM1.5D-G173 solar spectrum. This is not negligible and can cause a lower \( J_{sc} \) of the whole current-matched 4J solar cell, as was shown in Fig. 2.

1-sun I-V curves were also taken on these Ge solar cells. As expected, the \( V_{oc} \) of the Ge subcell exhibits changes too: the 1-sun \( V_{oc} \) drops from 232 mV to 177 mV when comparing the single-junction Ge subcell and the Ge subcell in the GaNAsSb/Ge cell, respectively. This \( V_{oc} \) loss is similar to previously measured in our lab for Ge subcells in 3J structures, and
also to the figures reported by Friedman and coworkers [4] for Ge subcell with typical and high emitter surface recombination velocities. This is in line with the idea that the compensated layer that is formed at the emitter surface, acting as an equivalent high surface recombination in the emitter, is the main cause of the Ge subcell performance degradation. In addition, and similarly as in the case of the EQE, the $V_{oc}$ does not exhibit any significant additional degradation during the growth of the top GaInP/Ga(In)As tandem, which, following with our reasoning, is consistent with the fact that the compensated region width does not noticeably change, as shown in Fig. 4. This also means that after a certain thermal load applied to the Ge subcell, its performance remains stable during the growth of the 4J structure.

**B. Degradation of the GaNAsSb subcell.**

The GaNAsSb subcell is submitted to ~2h 40 min of annealing at a temperature of 600 to 700 °C (see Table I). Annealing using engineered thermal loads is used in dilute nitride compounds to improve their electronic characteristics [5]–[9]. Hence, additional thermal loads applied to the GaNAsSb subcell could be expected to produce changes in its performance. Similarly as in the case of the Ge subcell, we studied the effect of this annealing on the QE and $V_{oc}$ of the GaNAsSb subcell. As commented before, we used for this study a single-junction GaNAsSb cell and annealed it using a thermal load equivalent to the case of a 4J structure. Two pieces of the same structure were used: one was directly processed into solar cell devices, and the other one was annealed before processing. During annealing, an additional doped capping layer was grown (~150 nm), to mitigate the possible degradation of the surface during annealing.

The QE and reflectance measurements are shown in Fig. 6. Firstly, a significant difference in the EQE for the short wavelength range is observed, which is due to the fact that the GaAs capping layer is thicker in the annealed sample. This causes also an important variation in the shape of the reflectance curve, which obscures the comparison of EQEs in the range of wavelengths of interest (~ 900 nm and above). However, this effect does not influence the IQE, which shows a similar shape in both the as-grown and annealed cases. The small IQE magnitude drop at the shorter wavelengths could be caused by the annealing, but is inside the combined uncertainty of the EQE and R measurements. Finally, a blue-shift
in the bandgap of dilute-nitride materials during annealing is reported in the literature [7], [9], [18]. This blue-shift is reported to be smaller in GaNAsSb as compared to other In-containing dilute nitride materials [19], but still we could observe it during the in-situ annealing right after the MBE growth of the GaNAsSb solar cell. However, no further blue-shift was detected after the annealing used to emulate the growth of the 4J structure, as shown in Fig. 6. This is in agreement with other works that describe a saturation of the blue-shift after some thermal load, and this behavior is actually used to determine the optimum annealing conditions to achieve the highest material quality [9], [20].

![Image of EQE, reflectance and IQE](image)

**Fig. 6.** EQE, reflectance and IQE of a GaNAsSb single-junction solar cell, and the same cell after annealing with a thermal load equivalent to its growth in a 4J structure.

The annealed GaNAsSb solar cells fabricated showed an unusually high series resistance due to a poor front contact. For this reason, the degradation of the $V_{oc}$ was studied using $I_{sc}$-$V_{oc}$ curves, since the series resistance was not high enough as to affect them. The result is shown in Fig. 7. The GaNAsSb solar cell exhibits a $V_{oc}$ of ~0.4 V at the 1-sun operation current density in the 4J. After annealing, a large voltage drop of ~140mV is observed. The ideality factor is 1.5 and is not altered significantly by the annealing.
C. Degradation of the tunnel junction.

The 4J solar cell structure developed comprises transparent and high performance AlGaAs:C/GaAs:Te and AlGaAs:C/GaInP:Te based tunnel junctions, whose details can be found in [21], [22]. These tunnel junctions exhibit peak current densities of 10 kA/cm² and 990 A/cm², respectively, for as-grown devices, and 2500 A/cm² and 235 A/cm² for annealed devices using a thermal load equivalent to the growth of a GaInP top cell (~30 min at 675 ºC). They also exhibit negligible voltage drops at usual operating current densities (~14 A/cm² for 1000 suns operation). However, the bottom AlGaAs:C/GaAs:Te tunnel junction in the 4J structure under study suffers annealing at temperatures ranging 460-700ºC during extended periods of time (almost 5 hours, see Table I). Therefore, a detrimental effect of this annealing could be expected and was investigated in this work.

The 4J solar cells have been measured under concentrated light using the flash-lamp method without spectral adjustment, to determine if any tunnel junction is limiting the performance at high concentrations. The 1mm² version of these solar cells, with a front grid suited for very high concentrations, were used. Concentrations up to ~ 1500 suns (limited by the flash tester) were used, and the results are shown in Fig. 8. As can be observed, the
shape of the I-V curves do not show any limiting tunnel junction effect, which means that the possible tunnel junction degradation is not severe enough as to affect the performance of the 4J solar cell under the high concentrations tested.

[Fig. 8. Concentration I-V curves of the 4J solar cell using the flash-lamp method with no spectral adjustment.]

6. Discussion

The 4J solar cell developed is, at this time, limited mainly by the poor quality of the GaNAsSb subcell. However, from the subcell and tunnel junction integration point of view, the analysis carried out concludes that the main issue is the photocurrent and $V_{oc}$ degradation of the Ge subcell, and the $V_{oc}$ degradation of the GaNAsSb subcell. The $J_{sc}$ of the Ge subcell is estimated to decrease by ~15%, while the $V_{oc}$ drop is of ~50 mV. This Ge subcell performance drop is obviously not acceptable and can drastically limit the efficiency achievable by the 4J solar cell as soon as a good quality dilute nitride subcell is obtained [11].
Diffusion of dopants and constituent elements is known to produce the observed degradation. In particular, in-diffusion of III-elements from the GaInP nucleation layer, which act as p-type dopants, has been found to produce a detrimental compensated region at the surface of the emitter. Preliminary SIMS measurements suggest that indium diffuses more into the emitter than gallium. This is probably due to a lower bond strength of InP than GaP, and a slightly higher diffusion coefficient of indium in germanium [23], [24]. On the other hand, a controlled diffusion of phosphorous is desired during the pre-nucleation step (exposure of the bare Ge surface to PH$_3$ at high temperature) in order to form the emitter of the Ge subcell. However, the subsequent thermal loads during the growth of the 4J structure produce a phosphorous drive-in effect, which is shown by the ECV graph in Fig. 4. This produces a thicker emitter and, possibly, a deterioration of its minority carrier properties. The fact that the EQE and $V_{oc}$ of the Ge subcell do not experience any significant change during the growth of the top GaInP/Ga(In)As subcells, even though the emitter doping profile changes but the compensated region does not, appear to suggest that the compensated region is the main cause of the performance degradation, acting as a minority carrier sink. This is consistent with a (equivalent) high emitter surface recombination velocity, as observed previously [4].

The study to mitigate the degradation of the Ge bottom cell is ongoing. Reducing the thermal load by using lower temperatures during the growth of some of the upper layers would be one solution. However this approach is constrained to temperature ranges that should not compromise the quality of the upper subcells. The annealing used to improve the performance of the dilute-nitride subcell has to be done at a temperature as low as possible [8]. Another less trivial approach consists of minimizing the in-diffusion of III-elements to avoid the formation of the compensated region at the surface of the Ge subcell emitter. For the growth conditions used in our 4J structure, indium diffusion appears to be the most significant, as explained above. Using GaAs as nucleation layer [25] would eliminate indium in-diffusion. However the diffusion of arsenic in Ge is an order of magnitude higher than for phosphorous [23], which gives rise to a much thicker emitter. Besides, gallium diffusion could probably be enhanced by a smaller bond strength of GaAs as compared to GaP. Nevertheless, the actual advantages of this approach remain to be tested. Other solutions consisting on using diffusion blocking structures are also under study.
Concerning the degradation of the $V_{oc}$ in the GaNAsSb, it is not surprising that an annealing of 2 hours and 40 min at ~ 600-700ºC affects the dilute-nitride material, according to the reports on the optimization of the intentional post-growth annealing used to improve the quality of the dilute nitride material. For example, Volz et al [9] reports a dramatic improvement in the photoluminescence intensity of the GaInNAs material grown by MOVPE after 30 min annealing at 700 ºC under TBA stabilization, but a similarly strong photoluminescence intensity drop after 2 hours of annealing. They also found that the optimum annealing conditions depend on the indium content. It is difficult, and is not the purpose of this paper, to deduce a quantitative and reproducible effect of annealing on dilute-nitrides, given the large variety of materials, growth conditions and thermal loads reported in the literature. The data we have available so far reveals that the optimum annealing conditions for our GaNAsSb material are 5 min at 700 ºC, and further annealing at ~600-700 ºC for 2 hours degrades it. It is possible that our dilute-nitride material is degraded due to the thermal load but also by the MOVPE environment, i.e., the presence of atomic hydrogen [26], [27]. Both thermal load and presence of atomic hydrogen are unavoidable in a MOVPE-grown structure. Therefore, the procedures needed to optimize the integration of the GaNAsSb subcell in the 4J structure will probably require designing an optimum combination of intentional annealing at the end of the dilute-nitride subcell growth with the unavoidable annealing during growth of the 4J. For example, a shorter intentional annealing combined with the annealing during growth of the upper layers in the 4J structure. On the other hand, the possible effect of the atomic hydrogen can possibly be reverted using post-growth annealing of the full 4J structure. The study of the effect of these methods is in progress and will be crucial in attaining a high efficiency 4J solar cell based on GaNAsSb material.

7. Conclusions

We have presented a GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell grown using combined MOVPE+MBE techniques. In its current development stage, this cell is limited by the performance of the dilute-nitride subcell. The bottom subcells and tunnel junctions are subjected to heavy thermal loads during the growth of the 4J structure. We have found that the Ge subcell in the 4J solar cell exhibits a significant degradation in $J_{sc}$ and $V_{oc}$ with respect to its performance as separate cells. The $V_{oc}$ of the GaNAsSb subcell also suffers a
significant drop. On the contrary, the tunnel junctions are not affected. The efficiency potential of this 4J architecture is compromised by the degradation of the Ge and GaNAsSb subcells. The development of mitigation strategies to control the diffusion of constituents and dopants in the Ge subcell, and the effect of annealing on the material quality of the GaNAsSb subcell is underway.

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References


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TABLE I
SUMMARY OF GROWTH TEMPERATURES AND TIMES, AND TOTAL ANNEALING TIME FOR EACH LAYER OF THE 4-JUNCTION STRUCTURE