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Plasma-enhanced chemical vapor deposition epitaxy of Si on GaAs for tunnel junction applications in tandem solar cells

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Abstract. We fabricated (n) c-Si/ (p) GaAs heterojunctions, by combining low temperature (∼175°C) RF-PECVD for Si and metal organic vapor phase epitaxy for GaAs, aiming at producing hybrid tunnel junctions for Si/III-V tandem solar cells. The electrical properties of these heterojunctions were measured and compared to that of a reference III-V tunnel junction. Several challenges in the fabrication of such heterostructures were identified and we especially focused in this study on the impact of atomic hydrogen present in the plasma used for the deposition of silicon on p-doped GaAs doping level. The obtained results show that hydrogenation by H₂ plasma strongly reduces the doping level at the surface of the GaAs: C grown film. Thirty seconds of H₂ plasma exposition at 175°C are sufficient to reduce the GaAs film doping level from $1 \times 10^{20}$ cm$^{-3}$ to $<1 \times 10^{19}$ cm$^{-3}$ at the surface and over a depth of about 20 nm. Such strong reduction of the doping level is critical for the performance of the tunnel junction. However, the doping level can be fully recovered after annealing at 350°C. © 2017 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JPE.7.022504]

Keywords: tandem solar cells; plasma-enhanced chemical vapor deposition; tunnel junctions; epitaxy; inverted metamorphic growth.

1 Introduction

This work is part of the French IMPETUS project [innovative multijunction combining metal organic vapor phase epitaxy (MOVPE) and plasma-enhanced chemical vapor deposition (PECVD) epitaxy at low-temperature for solar applications]. Here we present an approach to produce tandem solar cells that is based on the inverse metamorphic growth of crystalline silicon on GaAs.1-3

As shown in Fig. 1, the AlGaAs top cell is grown above 540°C by MOVPE on a lattice-matched GaAs substrate. Subsequently, the group IV cell (Si or SiGe) is obtained via heteroepitaxial deposition by low temperature PECVD (LT-PECVD). After the inverted metamorphic growth, the tandem solar cell is transferred to a low cost carrier. Following the removal of the GaAs substrate, the device process is finished on the low cost carrier involving metal contacts deposition, antireflection coating, and cell (mesa) definition. The main advantage of this approach is that the III-V subcell keeps its high quality as it is directly grown on a lattice-matched GaAs substrate. Moreover, at such a low growth temperature

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(175°C), we limit the thermal expansion issues. Last but not least, growing the group IV material on the III-V material prevents the polarity issues encountered in direct growth of III-V on Si.4,5

Previous work in the laboratory6 developed the growth of highly doped c-Si on c-Si substrate and on GaAs films, opening the path to the growth of III-V/Si hybrid tunnel junctions (TJ). The TJ is a crucial part of a multijunction solar cell, required to interconnect the subcells. While there is an abundant literature on III-V TJ,7,8 the use of hybrid TJ is limited to some works using a bonding approach.9,10 The direct deposition of Si on III-V has a huge potential and deserves to be considered for III-V/Si tandem solar cells. Indeed, possible defects or impurity incorporation at the III-V/Si heterointerface and therefore at the middle of the TJ could promote trap-assisted-tunneling. In our previous study, using numerical simulations,11 it was shown that even without defects at the interface, both (n) Si/(p) GaAs and (p) Si/(n) GaAs heterostructures can tunnel if the layers have a sufficient doping level (>2 × 10¹⁹ cm⁻³). Thus, in this study, we grew a hybrid (n) Si/(p) GaAs junction as well as reference (n) GaAs/(p) GaAs TJ, and investigated the current–voltage characteristics of the devices.

2 Experimental

In this work, it is proposed to grow and characterize heavily doped (n) GaAs/(p) GaAs junctions and (n) Si/(p) GaAs hybrid junctions, aiming at fabricating tunnel diodes. To grow the targeted device, MOVPE was used to grow highly doped GaAs on a (100) GaAs wafer. The used precursors are TMG₃ and AsH₃. SiH₄ and CBr₄ were added for the n-type and p-type doping, respectively. For each type of film, the highest doping level was achieved while maintaining high crystalline quality. Electrochemical capacitance–voltage (ECV) was used to calibrate the doping level in the p-type GaAs layers. This technique allows measuring the active dopant concentration and performing a depth profile of the carrier concentration. The highest doping level was 1 × 10²⁰ cm⁻³ for the p-doped GaAs:C and 1.2 × 10¹⁹ cm⁻³ for the n-doped GaAs:Si. It is challenging to achieve a higher n doping level with silicon as a dopant. This is due to its amphoteric nature, which means that the carrier concentration self-compensates above a doping level around 2 × 10¹⁹ cm⁻³.12 For the hybrid approach, doped Si films were deposited in a multiphase chamber PECVD reactor operated at a frequency of 13.56 MHz.13 First, in situ cleaning of the GaAs oxide was performed using a SiF₄ plasma, followed by Si deposition at very low temperature (175°C) using silane (SiH₄) and hydrogen (H₂) gas mixtures to which phosphine (PH₃) was added, leading to an n-type doping level of 1 × 10²⁰ cm⁻³. Diodes were then fabricated by standard technological steps in a clean room environment: photolithography, metallization, dry mesa etching of the epitaxial n-type silicon layer, and wet mesa etching of the GaAs.

Figure 2 shows schematic diagrams of the structures obtained after processing. Those structures were measured at room temperature in a four probes I-V bench, with a Keithley 2450 sourcemeter limited to 1A.
3 Results and Discussions

The structures were measured with a four-point probe technique to suppress the series resistance induced by the probes. To check reproducibility, the measurements were made on different diode designs (squares and circles of several sizes). The measured current density versus voltage curves, \( J(V) \), are displayed in Fig. 3.

The red curve (circles) corresponds to the standard GaAs/GaAs TJ. As expected, the curve exhibits the characteristic \( J(V) \) shape of a TJ with a peak current at low bias (\( \sim 0.1 \) V), then a valley and finally the classical diode current. A low resistance of \( 1.4 \times 10^{-2} \) \( \Omega \cdot \text{cm}^2 \) along with a peak tunneling current around \( 3 \) A/cm\(^2\) are obtained. This performance is reasonable considering that we reached a carrier concentration of only \( 1.2 \times 10^{19} \) cm\(^{-3}\) in the (n) GaAs, and it is compatible with its use in tandem solar cells working at low to medium concentration.

The hybrid junction however (black curve, triangles) led to a normal diode behavior without tunneling effect. The simulations previously presented\(^1\) predicted that with doping levels as high as \( 1 \times 10^{20} \) cm\(^{-3}\) in both parts of the junction, a tunneling peak current above 100 A/cm\(^2\) could be potentially achieved. Moreover, secondary ion mass spectrometry (SIMS) analysis of the device confirmed that we had a sufficient amount of C atoms in GaAs and P atoms in Si to provide the expected doping levels. However, the above characteristics do not meet the expectations. To explain these discrepancies, one can make the hypothesis that the doping level in the p-type GaAs is not as high as expected. Indeed, the doping level of the GaAs layer was calibrated separately on a test structure with thicker layers by using

![Fig. 2](image-url)

**Fig. 2** Test structures of the heterojunctions: (a) reference GaAs TJ, (b) hybrid silicon on GaAs, and (c) picture of the device after processing several diode designs.

![Fig. 3](image-url)

**Fig. 3** \( J-V \) curves of (n) Si/(p) GaAs (black triangles) compared with a (n) GaAs/(p) GaAs TJ (red circles). Orange squares represent the (n) Si/(p) GaAs after annealing at 350°C.
ECV measurements. However, in our final device, the GaAs layer was subject to the PECVD process of Si deposition, and therefore it was exposed to SiH₄ and H₂ plasma during the n-type silicon epitaxy. There are many reports on the effect of a H₂ plasma on doped GaAs. The diffusion of atomic hydrogen in the layer can lead to the formation of C-H complexes that neutralize the dopants. Rahbi et al.¹⁴ studied the acceptor passivation in p-type GaAs doped with different atoms: Zn, C, Si, and Ge. They exposed their samples to a hydrogen plasma at temperatures ranging from 150°C to 300°C for long durations (up to 8 h) and found a strong decrease in the doping level determined by Hall effect measurements. The decrease was about one-order of magnitude in the case of Si, Ge, and Zn doped GaAs. Their GaAs:C layers became highly resistive after plasma exposure. SIMS analysis confirmed that hydrogen had diffused in the p-type GaAs layers until a depth of 1 to 3 μm, depending on the hydrogen plasma exposure time and temperature.

In our case, the (p) GaAs layer was exposed to a H₂ plasma in the PECVD chamber for a much shorter time and lower temperature. It is thus important to verify if under our plasma conditions the dopants in the (p) GaAs are passivated, and to study how to recover from a drop in doping level. In our work, we investigate very thin layers and especially effects at the GaAs surface. This is not only important for understanding the behavior of hybrid p-n junctions, but it is also crucial for the final tandem device. Indeed, even for a standard III-V/III-V TJ in a III-V(MOCVD)/Si(LT-PECVD) tandem solar cell, the last layer before PECVD deposition will be highly doped and should be as thin as possible (below 30 nm).

To further examine the impact of the hydrogen plasma on (p) GaAs:C, three samples have been grown by MOVPE on (100) GaAs wafers with a buffer layer, followed by 500-nm-thick p-type layers with different nominal doping levels: 1 × 10²⁰ cm⁻³, 2 × 10¹⁸ cm⁻³, and 1.3 × 10¹⁷ cm⁻³ for samples A, B, and C, respectively. The three samples were exposed to very short (30 s) hydrogen plasmas in our PECVD reactor under the standard conditions of epitaxy: substrate temperature of 175°C, pressure of 2.1 Torr, and RF power of 10 W. To characterize the doping level, ECV measurements were performed before and after hydrogenation. Figure 4 shows the resulting carrier concentration profiles after H₂ plasma exposure. The dashed lines show the nominal doping levels of each sample.

On samples A and B the doping activity of carbon was widely reduced close to the surface of GaAs. The doping level decreases by one-order of magnitude in both samples despite the two-orders of magnitude difference in their nominal doping level. For sample A, initially doped at 1 × 10²⁰ cm⁻³, the 30 s hydrogen plasma exposure affected about 20 nm of the layer, while for sample B, initially doped at 2 × 10¹⁸ cm⁻³, the doping level was reduced over a thicker layer (about 100 nm). The thickness over which dopants are neutralized is inversely dependent on the initial C concentration. This result is consistent with the observation of Chevallier et al.¹⁵ in

![Fig. 4 Carrier concentration profiles of three GaAs(C) samples with different doping levels, after hydrogen plasma exposure. Dashed lines show the nominal carrier concentrations of each sample.](http://photonicsforenergy.spiedigitallibrary.org/pdfaccess.ashx?url=/data/journals/photoe/936171/)
GaAs doped with silicon. The neutralization of carbon is attributed to the fact that atomic hydrogen diffuses in the GaAs layer and forms complexes with carbon (C-H complexes) and thus deactivates it. The lower the concentration of carbon atoms, the deeper atomic hydrogen can diffuse. In the case of sample C, which has the lowest carbon concentration, the decrease in carrier concentration is smaller but happens over the whole 500-nm-thick layer. The effect of the H$_2$ plasma on lowly p-doped GaAs seems to be negligible at the surface. Table 1 summarizes the obtained nominal carrier concentration of the layer and its value at the surface of the GaAs after plasma exposure, where $N^0$ is the nominal carrier concentration, $N_{H_2}$ is the carrier concentration at the surface after plasma exposure, and $d$ is the depth to which the carrier concentration is modified.

This study on the effect of the H$_2$ plasma in our PECVD process shows that about one-order of magnitude of carrier concentration was lost at the surface of highly doped GaAs. In the case of our hybrid TJ, this happens at the interface between p-type GaAs and n-type Si, where the carrier concentration needs to be as high as possible to enable tunneling. With only $2 \times 10^{19}$ cm$^{-3}$ in the GaAs part of the TJ, no tunneling is expected,$^{11}$ which explains the diode behavior observed in Fig. 3 (black triangles).

Further experiments were designed to find out whether the electrical activity of acceptors can be restored by heat treatment. Thus, sample A has been annealed for 3 min at different temperatures from 250°C to 400°C after plasma exposure, and ECV measurements were performed after each annealing step. The results of this study are shown in Fig. 5.

![Fig. 5 ECV profiling of a p-doped GaAs layer grown by MOVPE ($1 \times 10^{20}$ cm$^{-3}$) as deposited (black diamonds) and after plasma exposure (full circles). The exposed samples have been annealed for 3 min at different temperatures: 250°C (open circles), 300°C (open triangles), and 350°C (red squares).](image)

### Table 1: ECV analysis results on p-type GaAs:C doped at different doping levels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N^0$ (cm$^{-3}$)</th>
<th>$N_{H_2}$ (cm$^{-3}$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1 \times 10^{20}$</td>
<td>$2 \times 10^{19}$</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>$2 \times 10^{18}$</td>
<td>$1 \times 10^{17}$</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>$1.3 \times 10^{17}$</td>
<td>$8.5 \times 10^{16}$</td>
<td>500</td>
</tr>
</tbody>
</table>
shows a better recovery of the doping level at the surface, which reaches $6 \times 10^{19}$ cm$^{-3}$. After a 350°C annealing, the doping level at the surface is almost fully restored. The same study has been performed on sample B (not shown here), and a complete recovery of carrier concentration was also obtained after heating at 350°C.

The previous experiments performed on p-type GaAs doped with carbon helped us to understand what happened at the interface of our hybrid device. Thirty seconds of H$_2$ plasma exposure are enough to reduce the doping level by one-order of magnitude, but this effect can be recovered by annealing. Thus, we propose to anneal the device at a temperature of 350°C to restore the doping level of the GaAs layer. The J(V) curve of the hybrid device after annealing is plotted in Fig. 3 (orange squares). It exhibits a linear behavior, with a very low resistance of $9 \times 10^{-4}$ Ω cm$^{-2}$. The best III-V TJ reported in the literature shows resistances below $10^{-4}$ Ω cm$^{-2}$ for high concentration applications.\textsuperscript{16} The resistance of our hybrid devices is thus very promising for our low concentration application. As a matter of fact, as judged by the slopes at the origin, the resistance of the hybrid device (orange squares) is smaller than that of the GaAs:Si/GaAs:C TJ grown in our laboratory (black triangles, $1.4 \times 10^{-2}$ Ω cm$^{-2}$). However, the typical negative region of a TJ is not visible, which could be caused by a high dislocation density in the layers.\textsuperscript{17}

4 Conclusion

In summary, we have presented a first hybrid PECVD Si on MOVPE GaAs device aiming at obtaining a hybrid TJ. Heavily n-doped crystalline silicon was grown successfully by PECVD at 175°C on a p-doped GaAs layer. The electrical results of the fabricated device unexpectedly showed a diode behavior instead of a TJ behavior, meaning that the actual doping level in the device was not as high as the nominal one. We highlighted the strong effect of the hydrogen plasma during the PECVD process: 30 s of H$_2$ plasma at 175°C are sufficient to reduce the doping level of a heavily doped p-type GaAs by a factor of 10, due to the neutralization of carbon dopants after formation of C-H complexes, thus preventing the hybrid device from tunneling. This neutralization can be recovered after a 350°C annealing. Highly doped GaAs:Si/GaAs:C junctions were also processed and showed good tunneling properties, suitable for a III-V/Si tandem solar cell.

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References


Gwénaëlle Hamon received her master’s degree in physics and nanosciences from Phelma–Grenoble Institute of Technology, France, in 2014, specializing in optics and microelectronics. Currently, she is working toward the PhD at Ecole Polytechnique in the joint research team between TOTAL and LPICM, under the supervision of P. Roca i Cabarrocas. She works on III-V/Si tandem solar cells using low temperature plasma-assisted epitaxy of Si on MOVPE grown III-V materials.

Nicolas Vaissiere was qualified to PhD level in 2014 from ENS Cachan. He made the first x-ray detector based on epitaxial diamond by BEN-MPCVD at CEA. During one year at GEMaC/CNRS as a postdoc researcher, he succeeded in adapting MOCVD technology on a commercial MPCVD reactor for n-type doping of diamond. Currently, he is at LPICM/Ecole Polytechnique working on the epitaxial integration of Si(Ge) on III-V at low temperature PECVD for tandem solar cells.

Romain Cariou studied physics at ENS Cachan, and Pierre-and-Marie-Curie University, France. He holds his master’s degree from Ecole Centrale Paris and his PhD from Ecole Polytechnique, since 2014. His PhD research work was performed with the Laboratory of Physics of Interfaces and Thin Films (LPICM-CNRS) and Alcatel-Lucent Bell Labs France (III-VLab). In 2015, he joined the Fraunhofer Institute for solar energy systems, Freiburg, Germany, with a Marie Curie project focusing on III-V/Si multijunction cells.

Raphaël Lachaume received his MS degree in microelectronics and nanotechnology from Strasbourg University and Ecole Telecom Physique Strasbourg in 2010. Then, he undertook his PhD in CEA Leti in collaboration with CEA INES on high efficiency heterojunction solar cells. Since 2014, he has been working on advanced electrical characterization and modeling for next generations of solar cell devices in Group of Electrical Engineering, Paris (GeePs) and more recently in Institut PhotoVoltaïque d’Ille de France.

José Alvarez received his PhD from the University of Pierre-and-Marie-Curie University in 2004. Thereafter, he joined the International Center for Young Scientist at NIMS in Tsukuba, Japan. Since October 2005, he has been working as a researcher at the laboratory GeePs, Gif-sur-Yvette, France. His current fields of interest are linked to the scanning probe and confocal microscopy characterization techniques applied to materials (silicon-based structures, III-V materials) and devices.
Wanghua Chen received his PhD from the University of Rouen, Normandy, France, in 2011. He joined LPICM, CNRS, Ecole Polytechnique, France, as a postdoctoral researcher, in 2013. He has made a series of original research works on chemical vapor deposition systems, semiconductor nanowire, low-temperature semiconductor epitaxial growth, and passivation of c-Si solar cells. He has published more than 25 papers in *Nature Communications*, *Progress in Photovoltaics*, *Applied Physics Letters*, and other peer-reviewed journals.

Jean-Paul Kleider holds his engineering degree from Ecole Supérieure d'Electricité in 1984 and received his PhD from the University Pierre et Marie Curie (Paris VI) in 1987. He is leading the physics and electronics of materials, devices, interfaces, and contacts division at GeePs, where he works as a CNRS director of research. He has extensive experience in the field of electrical and optoelectronic characterization and has published over 240 papers.

Jean Decobert is epitaxy team leader at III-V Lab. He has been working on epitaxial growth since 1987. He received his PhD in microelectronics from the University of Lille and joined France Telecom in 1993. In 2004, he joined the III-V lab, where he was in charge of MOVPE for optoelectronic applications, with research activities on photonic integrated circuits. Actually, he focused on selective area growth technique, III-V integration on silicon and photovoltaic tandem solar cells.

Pere Roca i Cabarrocas received his PhD from the University Paris VII in 1988. After a postdoc at Princeton University, he joined the LPICM, where he holds a position as a CNRS director of research. He has a long experience in the plasma deposition of silicon based thin films. He was the recipient of the silver medal from CNRS in 2011. He has over 450 papers in peer-reviewed journals and holds 34 patents.