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One obstacle for the development of nanowire (NW) solar cells is the challenge to assess and control their nanoscale electrical properties. In this work a top-cell made of p-n GaAs core/shell NWs grown on a Si(111) substrate by Molecular Beam Epitaxy (MBE) is investigated by high resolution charge collection microscopy. Electron Beam Induced Current (EBIC) analyses of single NWs have validated the formation of a homogeneous radial p-n junction over the entire length of the NWs. The radial geometry leads to an increase of the junction area by 38 times with respect to the NW footprint. The interface between the NWs and the Si(111) substrate does not show any electrical loss, which would have led to a decrease of the EBIC signal. Single NW I-V characteristics present a diodic behavior. A model of the radial junction single NW is proposed and the electrical parameters are estimated by numerical fitting of the I-Vs and of the EBIC map. Solar cells based on NW arrays were fabricated and analyzed with EBIC microscopy, which evidenced the presence of a Schottky barrier at the NW/ITO top contact. Improvement of the top contact quality is achieved by thermal annealing at 400°C, which strongly reduces the parasitic Schottky barrier.

Introduction

To overcome the Shockley-Queisser limit of a photovoltaic device¹, the approach which so far has given the best results in terms of conversion efficiency is the association of active materials with different band-gap energies in multi-junction devices (Tandem Solar Cells, TSC). This approach reduces the thermalization and transmission losses. Thin film three and four junction solar cells under light concentration hold the actual photovoltaic efficiency records of 44.4% and 46.1%, respectively^{2,3}. These devices have a very complex structure with up to ten layers for each sub-cell, which makes their fabrication very challenging. The efficiency of planar multi-junction solar cells strongly depends on the material quality, in particular, on the defect density in the active regions. Lattice matching is thus required to stack different layers of high material quality, imposing a significant constraint on the material combinations and

increasing the complexity of fabrication process. The necessity of expensive substrates (Ge or III-V) and the high production cost are hindering the widespread use of this technology. An alternative actively explored architecture is based on III-V on Si tandem cells. It targets somewhat lower efficiencies than three and four junction tandems, however it offers a significant enhancement with respect to a bare Si device^{4,5} and can benefit from the maturity of the Si PV technology.

The optimal parameters for III-V/Si tandem solar cells have been largely investigated. Numerical simulations indicate that an optimal band gap of the top cell of 1.7 eV can lead to an overall efficiency up to 42% under 1 sun illumination^{4,6}. III-V ternary alloys (InGaP, GaAsP, AlGaAs, InGaN) are necessary to match this optimal band gap value. GaAs has also been proposed as a top cell material to reduce the production cost with respect to devices based on In-rich materials. The realization of III-V/Si dual junction solar cells using InGaP and GaAs materials as a top cell has been recently reported in literature, comparing the performance of the two devices⁷. Although the ternary alloy presented a band gap closer to the optimal one, it has been shown that the GaAs/Si tandem device exhibits an efficiency around 32.8% under 1-sun illumination while the InGaP/Si tandem solar cell

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showed a slightly lower efficiency (32.4%) in the same testing condition. This work points out the advantage of using a well-known binary material such as GaAs which can offer a high material quality. Nevertheless, implementation of III-V materials on Si offers plenty of challenges to achieve both a technological reliability and an economic viability. For this reason both wafer bonding and direct III-V on Si growth are explored^{5,8}, each of them presenting advantages and drawbacks. For the direct growth, the main difficulties are related to the lattice mismatch and the formation of anti-phase domains when integrating a polar III-V material on a non-polar Si crystal^{9,10}.

In this context, the development of nanowire (NW) based devices can address these challenges. On one hand, the use of III-V NWs in place of a thin film allows to stack lattice-mismatched materials (and in particular to integrate III-Vs on Si) without forming threading dislocations by lattice misfit relaxation at the interfaces¹¹. This unique property of NWs enables the use of cheap substrates for the growth of materials of high crystal quality. In addition, NW arrays have very attractive optical properties such as a small optical reflectance and enhanced light diffusion^{12,13}, leading to an increased absorption in comparison to thin films. Therefore, a reduction of the active material volume necessary for efficient absorption and thus a decrease of associated material costs is predicted for NW solar cells. On the other hand, new scientific and technological challenges have to be faced to demonstrate high-efficiency NW solar cells. These are namely the control over the uniformity of the NWs morphology and density, a single crystal phase without stacking fault defects, controlled and uniform doping, low surface recombination velocities for minority carriers^{9,14}. At the present moment, InP and GaAs NW solar cells have been demonstrated with efficiencies ranging from 13.8% to 17.8%^{15–17}. Concerning ternary compounds, control over the composition of the alloy in NWs is still an open challenge, and research in this field is very active. For this reason, GaAs/Si NW tandem solar cells have been proposed as a compromise between the performing requirements (estimated maximum efficiency < 30%^{18,19}) and technological issues. The realization of this device has been reported for the first time in 2015, achieving an efficiency of 11.4%²⁰. To have a comprehensive understanding and to boost the performance of NW-based devices it is necessary to characterize the electrical properties down to the nanoscale level.

Standard characterization techniques for thin film solar cells can be used to assess the global performance of the devices, but do not give a full picture of the physical processes occurring in individual NWs.

Probing individual NWs and in particular their electrical properties usually involves destructive processes and time- and energy-consuming fabrication steps to realize contacts to these nanoobjects^{21,22}. In this context, characterization methods based on scanning probe techniques appear highly appealing due to the possibility to probe individual nano-objects without the necessity of lithographically designed contacts. An example is given by the c-AFM analysis, which allows to scan large surfaces and assess the electrical properties of single NWs combining topological and current maps^{23–25}.

Among the different scanning probe techniques, electron beam induced current (EBIC) microscopy has been widely used in optoelectronics, and in particular solar cells, for more than thirty years²⁶. In 2D solar cells, EBIC was used to probe the electrical activity of the devices with a high resolution, to extract material parameters and to detect failures induced by material defects. This technique offers a nanoscale resolution and therefore is ideally suited for nanostructured solar cell characterization.

In this work, we present an investigation of the electrical properties of self-catalyzed p-n GaAs core/shell NWs by means of EBIC mapping. The approach used in this work allows a process-free characterization thanks to the use of nano-manipulators integrated into the SEM chamber which can be used to address individual NWs in an array with a high measurement throughput. Hence, the samples can be investigated “as-grown”, lowering significantly the time needed for the characterization and eliminating any artifact arising from the fabrication steps.

The NWs discussed in this work contain a radial p-n junction and were grown on Si(111) by molecular beam epitaxy (MBE). Their structural and optical properties were characterized by power-dependent low temperature photoluminescence (PL) and transmission electron microscopy (TEM). EBIC mapping performed on single NWs showed that the current collection occurs homogeneously over the entire length of the NWs, indicating a good homogeneity of the radial junction as well as a high conductivity of the p-doped core. No EBIC signal was observed at the NW/substrate interface showing a good carrier collection and the absence of a

parasitic diode at this position. The experimental results are fitted by a simulation based on an equivalent circuit for single core/shell NWs. The electrical parameters of the junctions are estimated. After encapsulation and ITO top contact deposition, EBIC microscopy has been performed to investigate at the nanoscale the contact properties. A thermal treatment is required to improve the electrical access, as revealed by EBIC analysis.

Results and Discussion

Growth and structural characterization

Self-catalyzed NWs were grown by solid-source molecular beam epitaxy (ss-MBE) using the vapour-liquid-solid (VLS) mechanism for the core and a vapour-solid (VS) mechanism for the shell. The growth was carried out on an epi-ready Si(111) substrate, with a SiO₂ surface layer whose thickness is estimated around 2 nm. The Si substrate was p-doped with boron with a resistivity in the 0.02–0.06 Ω·cm range.

In order to remove possible contaminants from the surface, the substrate was sonicated in acetone and ethanol for 10 minutes and dried under a nitrogen flow. It was then degassed at 200 °C in ultra-high vacuum and introduced inside the MBE reactor.

The structure of the NWs consists in a p-GaAs core with a n-GaAs shell forming the active p-n junction in GaAs, covered with passivating Al_xGa_{1-x}As and GaAs shells. A schematic of the NW structure, with the profiles and lengths of the different parts deduced from the TEM analysis (see after), is shown in Figure 1a.

Core and shells were p- and n-doped using Be and Si, respectively. The Be flux used for the core corresponds to a nominal doping concentration around $2\text{--}3 \cdot 10^{18} \text{ cm}^{-3}$ in 2D GaAs layers grown at 0.9 μm/hr.

Similarly, the one adopted for Si in the same conditions corresponds to a nominal doping concentration of $5\text{--}6 \cdot 10^{18} \text{ cm}^{-3}$.

Based on the data reported in the literature^{27–29} the doping level of the p-GaAs core is expected to be equivalent to the nominal value of $2\text{--}3 \cdot 10^{18} \text{ cm}^{-3}$. On the contrary, the doping level of the n-AlGaAs shell is supposed to be higher than the nominal one and estimated in the $1.5\text{--}1.8 \cdot 10^{19} \text{ cm}^{-3}$ range, since in our conditions the typical radial growth rate is about 0.75 Å/sec (0.27 μm/hr), i.e. three times lower than for 2D GaAs layers.

The NWs were grown as following: one monolayer (ML) of Ga was deposited on the substrate at 520 °C to form nano-droplets, then the substrate temperature was increased to 610 °C to grow the NWs by opening the Ga and As₄ fluxes. The p-doped GaAs core was grown for 10 minutes with As₄ and Ga fluxes equal to 8.0 Å/sec and 1.4 Å/sec (quoted in units of equivalent 2D growth rates of GaAs layers measured by RHEED oscillations)²⁸, respectively, and corresponding to a V/III flux ratio equal to 5.7. The Ga droplets at the top of the NWs were afterwards consumed by exposition to As₄ flux only (without Be flux), while decreasing the temperature to 460 °C. The radial p-n junction was obtained by growing a n-doped shell around the p-doped core at 460 °C. A second n-doped shell of Al_xGa_{1-x}As (with an Al flux equal to 1.4 Å/sec, corresponding to a nominal composition of Al_{0.5}Ga_{0.5}As) was grown so as to prevent carrier recombinations at the GaAs NW surface, thus enhancing the photoluminescence efficiency,³⁰ and a thin n-doped GaAs shell was finally added to prevent the oxidation of Al.³¹ The three shells were grown using the same Ga and As₄ fluxes adopted during the growth of the core, for a total growth time of 23 minutes, divided as follows: 10 minutes of n-GaAs, 10 minutes of n-Al_xGa_{1-x}As and 3 minutes of n-GaAs. Throughout all the growth, the substrate was rotated at 3 rpm.

The SEM image of p-n core-shell GaAs NWs is shown in Figure 1b. The NWs present a high vertical yield (96 %), a high density ($6.6 \mu\text{m}^{-2}$ for vertical ones), and good morphological properties, with lengths of $1.1 \pm 0.2 \mu\text{m}$ and diameters of $85 \pm 5 \text{ nm}$. Considering that the diameter of core-only NWs grown in the same conditions is equal to $40 \pm 3 \text{ nm}$, we can estimate the thicknesses of the n-GaAs, n-Al_xGa_{1-x}As and final n-GaAs shells to be about 7 nm, 14 nm and 2 nm, respectively.

Figure 1: a) Schematic of the p-n core/shell GaAs NW structure. The profiles and lengths of the different parts of the NW are deduced from the TEM analysis. b) SEM image of the NWs (tilt angle 45 °).

Figure 2a shows a HAADF-STEM image (with [11-2] zone axis) of a typical NW whose length is equal to about 1.25 μm and diameter to 90 nm. By combining TEM imaging of the NW crystal structure with [11-2] zone axis (Figure 2a) and with [1-10] zone axis (not shown), it is possible to recognize five different zones along the NW, corresponding to different growth stages: the first one (715 nm long, marked with a red arrow) corresponds to the VLS growth of the p-GaAs core and presents a Zinc-Blende (ZB) structure with some stacking faults (twins). These stacking faults can be due to the relatively high V/III flux ratio used for the growth of these NWs. The succeeding zone (210 nm long) is the sequence grown during the Ga droplet consumption, with a first ZB

segment with a high density of stacking faults, then a second segment with a Wurtzite (Wz) structure³². Then, it can be seen again three highly stacking-faulted ZB zones formed at the tip of the NW during the radial growth of the n-GaAs and n-Al_xGa_{1-x}As/n-GaAs shells, with lengths equal to 180, 95 and 27 nm, respectively, which provide a substantial contribution to the overall length of the NW. We can note that the shell thickness strongly depends on the plane orientation: as a matter of fact, the thickness of the shells grown on the {111} top facets is bigger than the thickness measured on the {110} lateral facets, since the latter ones are less exposed to the III element flux.

Figure 2: a) HAADF-STEM image (with [11-2] zone axis) of a typical p-n core-shell GaAs NW with Al_xGa_{1-x}As/GaAs passivating shells, showing the different zones along the NW. Inset: magnified image showing the thickness of the Al_xGa_{1-x}As and final GaAs shells and the composition inhomogeneity in the Al_xGa_{1-x}As shell due to the presence of stacking-faults. b) EDX mapping of Al and Ga. Inset: the corresponding HAADF-STEM image (with [11-2] zone axis). The scale bars are 50 nm.

Further information about the composition of the shells were collected by EDX analysis of the NW as shown in Figure 2b. In particular, the ternary alloy is revealed to have an actual composition between Al_{0.52}Ga_{0.48}As and Al_{0.57}Ga_{0.43}As depending on the zone, in any case very close to the target value of Al_{0.5}Ga_{0.5}As. Finally, the HAADF-STEM image also gives information about the thickness of the different shells. As measured from Figure 2a inset, the passivating Al_{0.5}Ga_{0.5}As and GaAs shells are 15 nm- and 1.8 nm-thick, respectively. Considering that the growth rate for Al_{0.5}Ga_{0.5}As was

twice the one adopted for n-GaAs, it is therefore possible to assume that the thickness of the n-GaAs shell around the core is 7.5 nm. These values are very close to the ones expected from SEM estimation, and considering that the overall diameter of the p-GaAs core plus the n-GaAs shell is 55 nm, they are also consistent with the assumption of a p-GaAs core diameter of 40 nm.

Optical properties of p-n core-shell GaAs NWs were studied by photoluminescence (PL) spectroscopy at 13 K. The sample was mounted in a closed cycle helium cooled cryostat and optically pumped by a 532 nm cw diode-

pumped solid-state laser ($P=70$ mW, $200\ \mu\text{m}$ in diameter spot size). The detection was provided by a nitrogen-cooled silicon CCD detector coupled to a monochromator. The PL spectrum presents two peaks (Figure 3a): the peak at 1.37 eV is attributable to GaAs and the one at 1.67 eV to the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell. Two hypothesis could explain the observation of the GaAs peak at 1.37 eV, i.e. 0.14 eV below the usual bandgap of undoped ZB GaAs at cryogenic temperature. By comparing PL spectra recorded using different excitation powers we can see a strong blue-shifted of the low energy peak as the power is increased (Figure 3b). This behaviour is usually interpreted as a signature of carrier separation or state filling. As a first hypothesis, the emission is related to the p-doped GaAs core and to the ZB/Wz mixed structure (due to the presence of stacking faults) of the NWs. The low energy emission would be the consequence of the mixed structure and Be doping levels which can both induce potential fluctuations in the GaAs material along and perpendicularly to the NW axis. To support this hypothesis, we can mention that PL emission below 1.3 eV has already been reported for Si doped GaAs NWs where the amphoteric behavior of the Si dopant increases the potential fluctuations.³³ The second hypothesis is related to a band bending along the radial axis as a consequence of the p-n GaAs junction. The electrons are localized at the n-doped GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ interface whereas the holes are in the p-doped GaAs core. To support this hypothesis, we can mention that such a band bending has already been observed for GaAs/AlGaAs core-shell NWs even in the case of an undoped heterostructure.³⁴

Figure 3: a) PL spectrum of p-n core-shell GaAs NWs with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ /GaAs passivating shells at $T=13$ K, with an excitation power $P=70$ mW, b) PL spectra at 13 K as a function of the excitation power from 0.7 to 70 mW.

In the case of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ peak, the PL emission is likely caused by donor-acceptor transitions or localized states induced by compositional inhomogeneity inside the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell as observed on the magnified TEM image with $[11-2]$ zone axis (inset of Figure 2a), and as already mentioned by several groups.^{35,36}

Electrical Measurements on Single NWs

Single NW characterization is performed in a Hitachi SU-8000 SEM, where electrical contact to single NWs is achieved using Kleindiek PS4 nano-manipulators equipped with $100\ \text{nm}$ radius tungsten tips. Prior to the measurement, no surface treatment is performed on the NWs hence they are measured “as-grown”. I-V measurements are performed by a Keithley 2636 source-meter coupled with a LabView acquisition software, with a measured noise level lower than $0.1\ \text{pA}$ in these experimental conditions. The same setup is used to study the internal electric field in the NWs by means of electron beam induced current (EBIC) microscopy. In EBIC microscopy electron-hole pairs are locally generated by the electron beam. In structures with a built-in internal field, the electron-hole pairs created close to the field region can be separated and collected producing a measurable current^{37–39}. EBIC measurements were performed at $2\ \text{kV}$ acceleration voltage and $37.7\ \text{pA}$ injected current. Injected current is measured by means of a Faraday cup. An external bias ranging from $-1.5\ \text{V}$ to $+1.5\ \text{V}$ is applied through a Stanford SR560 preamplifier controlled by a Gatan DigiScan system. More details about the set-up can be found in previous works^{39,40}. Both I-V measurements and EBIC maps are acquired on 16 different NWs, chosen on different areas of the sample. The results described in this work are representative of 87% of the investigated NWs. Figure 4 displays the electrical characterizations and the EBIC maps of the same single NW contacted on its top. As seen in panels c) – e), the NW is slightly bended by the force exercised by the nanomanipulator (which is necessary to establish a stable electrical contact). The I-V curves (Figure 4a) show a diodic behavior without external excitation, characterized by a very weak leakage current, which is below the sensitivity of our set-up in the investigated voltage range. The diode opening voltage is around $0.75\text{--}0.9\ \text{V}$. Under electron irradiation, the induced current can be detected under zero or reverse bias, with a value around $0.60\ \text{pA}$, which only weakly depends on the reverse bias. In the forward regime, the I-V curves under excitation are characterized by an open circuit voltage (V_{oc}) around $0.36\pm0.04\ \text{V}$ and an

increased slope of the I-V curve indicating a decrease of the series resistance (Figure 4b).

We note that for the used excitation conditions single NWs demonstrate a fill factor FF ~40% (FF=32% in the example of Figure 4b). Even though this result is obtained under an electron beam excitation and thus no PV conversion efficiency can be extrapolated, the present analyses show that the p-n junction is electrically active and can efficiently separate generated carriers. The homogeneity of the current generation in the p-GaAs core/ n-GaAs shell structure is analyzed by EBIC mapping as displayed in Figure 4c, d and e. Each panel shows an SEM image and a corresponding EBIC map at a fixed external bias. When a negative bias is applied (Figure 4c), the EBIC map shows a pronounced negative current induced by the p-n junction (appearing as a black

contrast), coherently with the previously described I-V curves.

The collected current from the radial junction can be observed also without any applied bias (Figure 4d), even though the signal-to-noise ratio strongly decreases indicating the presence of a variable series resistance (possible arising from the Schottky nature of the tip to NW contact as discussed below). When a forward bias is applied (Figure 4e), the p-n junction becomes flattened and its signal disappears. Only a weak EBIC signal of a positive sign (appearing as a white contrast) is detected at the tungsten tip/NW interface due to the presence of a Schottky contact. The band bending at the Schottky contact to the n-doped shell is expected to have the opposite sign with respect to the internal field in the p-n junction, in agreement with the observation of the opposite sign of the induced current.

Figure 4: a) I-V curves of a single NW in the dark (black) and under electron beam exposure (red): the red letters indicate the bias conditions corresponding to EBIC maps shown in c), d) and e); b) Zoom of the I-V curve: the red dotted line represents the interpolation of the experimental data acquired under electron irradiation; c), d), e) SEM images and corresponding EBIC maps respectively at $V_{bias} = -1.5 \text{ V}$, $V_{bias} = 0 \text{ V}$, $V_{bias} = +1.5 \text{ V}$. On the right of each map, the grey coded current scale is displayed.

By extracting the EBIC profile along the axis at -1.5 V bias (Figure 5) it is possible to analyze the current collected as a function of the position. In the top part, the collected current increases from the manipulator towards the NW base indicating a diffusive transport regime (region I). This is coherent with the presence of an axial p-n junction formed due to the shell coverage of the NW top. It is difficult to estimate the minority carrier diffusion length in the axial direction since the top region contains a complex capping structure with a large number of stacking faults. Nevertheless, the EBIC profile shows that the carriers can be collected efficiently also in this top segment despite the high density of stacking faults in this region. This indicates that carrier losses in the top part of the NW are not significant. Moreover, since the stacking faults are perpendicular to the NW axis, it is reasonable to assume that the diffusion length in the radial direction is not lower than the value along the axial direction. Since the NWs radius is around 40 nm, the observation of the diffusive transport over 100 nm axial top segment ensures an efficient collection of generated charges over the entire NW diameter.

The collected current is constant along the whole length of the NW, indicating an efficient radial drift of the induced carriers and their transport by the core and the shell.

The portion of the NW with the homogeneous current collection (section III) represents about 80% of the total length corresponding approximatively to the length of the NW core (p-GaAs core + i-GaAs segment) measured by TEM.

Figure 5: The EBIC profile along the NW axis at -1.5V bias applied compared to the schematic of the NWs. The green dotted circle indicates the interface between the GaAs core/shell junction and the SiO_x layer and the induced current collected in this area. Dotted lines are used to define the three transport regime discussed in the text (I: diffusive transport; II: mixed diffusion and drift transport; III: carriers' drift to the junction).

This analysis is important to assess the material quality. In fact, a homogeneous collection of carriers is observed along both the p-GaAs core grown via the VLS mechanism with stabilized Ga droplet and the nominally undoped GaAs segment grown during the droplet consumption. The present observation indicates the possibility to achieve a high efficiency collection of carriers over a large junction area. In fact, this portion corresponds to a cylindrical junction area with an extension 38 times higher than the NW footprint. This evidence underlines the advantage of the core/shell architecture with respect to the axial one, since the depleted region can be increased by almost 40 times with the same amount of material.

It is worthy to mention that no reduction of EBIC current is observed in the vicinity of the interface with the substrate (green dashed oval in Figure 5). This would have been the case if the NW/substrate interface was subject to strong non-radiative recombinations due to poor crystalline quality close to the NW substrate. In fact, defects at the NW/substrate interface would lead to a reduction of the induced current in the wire towards the substrate. If parasitic defective crystals growing on the substrate close to the wire are electrically connected to its base, it would yield a similar EBIC reduction towards the base.

The constant EBIC current profile down to the NW/substrate interface ensures also a good quality of the p-n GaAs/ SiO_2 interface. The effect of non-radiative recombination at the p-n GaAs/ SiO_2 interface has been theoretically analyzed by Maryasin et al.⁴¹. The authors showed that the non-radiative losses at this interface would lead to a strong decrease of the collected current and thus to a strong decrease in the overall efficiency of the devices. In absence of strong EBIC current variation near the interface, we can assess that this interface does not introduce additional losses within the EBIC sensitivity limit. Moreover, no parasitic EBIC signal is observed at the NW/p-Si substrate interface for any applied bias (as seen in Figures 4c-e). Considering both observations, it is likely that no electric field is present in the interface region independently on the applied bias. The band alignment between the p-Si and the p-GaAs eventually separated by a residual discontinuous SiO_2 layer has not been analyzed in the literature. However, the present observations show that this interface has a good conductivity since it does not prevent the collection of the induced signal. We can conclude that there is no potential barrier at the NW core/substrate interface. In addition, this evidence is coherent with the low leakage current showed in the I-V characteristic.

The electrical parameters of a single NW can be extracted by fitting the single NW I-V characteristics (in the dark

and under electron exposure) and the EBIC profile. The simulations allow to estimate the electrical resistance of the core (R_{core}) and of the shell (R_{shell}) separately. In fact, the I-V measurements contain information on the total electrical resistance and the EBIC profile contains information on the relative resistance of the core and the shell, as shown in ref.²².

The I-V curves and EBIC profile are numerically fitted with the following model. The simulation is based on a multi-diode equivalent circuit (Figure 6) which represents the radial NW junction as an ensemble of a large number of sub-cells.

Each sub-cell consists of a series resistance (R_s), a shunt resistance (R_{sh}), an ideal diode (described by its saturation current I_{sat} and its ideality factor η) and a current generator to account for the EBIC current (I_{illum}) generated under electron beam irradiation (Figure 6). Without electron irradiation $I_{\text{illum}} = 0$. The different sub-cells are connected by the core (R_{core}) and shell (R_{shell}) resistances. For a realistic modeling of a continuous radial junction, the number of sub-cells in the circuit is increased until the resulting values per unit length remain unchanged within the desired accuracy. A total number of 100 sub-cells was fixed in the following discussion. For further details on the model please refer to ref.²².

The position of the n-contact on the shell depends on the position of the manipulator tip on the NW.

Due to the complexity of the experimental setup, some assumptions are needed:

- The electrical resistance is given only by the resistances of the equivalent circuit. This means that the model does not account for any resistance external to the NW (contact resistance, substrate resistance, set-up resistance and so on).
- No rectifying behavior is considered at the NW/substrate interface: even though the NW and the substrate form a hetero-interface, the absence of the EBIC signal at this position indicates that no rectifying phenomena occur.
- The Schottky barrier at the NW/tip interface is neglected. Neglecting an external rectifying element could lead to a difference in the junction parameters (I_{sat} , η , R_{sh}) under irradiation.

The simulation enables the fitting of the I-V curves acquired in the dark and under electron irradiation shown respectively in Figure 7a and b, respectively.

The experimental and simulated EBIC profiles along the NW axis are displayed in Figure 7c and d, respectively. The fitting parameters are reported in Table 1.

A good agreement between the experimental and simulated I-V characteristics and EBIC profiles was found and the extracted parameters can be used to describe the electrical parameters of the NW.

Comparing the diodic parameters used to fit the I-V curves in the dark and under electron beam irradiation, it is clear that the radial junction has good rectifying properties, described by a very low value of the saturation current ($I_{\text{sat}} < 10^{-13} \text{ A}$) and an extremely high shunt resistance ($10^6 \text{ G}\Omega$). These results are consistent with the low leakage observed at the single NW level. As discussed previously, this observation validates the absence of additional leakage at the NW/substrate interface, where the n-GaAs shell may come in contact with the p-Si substrate.

The estimated ideality factor η is quite high both in the dark and under electron beam irradiation. This is ascribed to the presence of a parasitic Schottky barrier at the manipulator/NW contact interface. Moreover, the variation of the ideality factor when the system is exposed to the electron flux is coherent with the modification of this Schottky barrier. The core and shell resistances extracted from the fitting are very high. Indeed, a simple estimation considering a cylindrical geometry gives a total resistance of a few k Ω (considering mobility values of $\mu_p = 140 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_n = 1430 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at the estimated doping levels)^{42,43}. In addition, core and shell resistance values do not vary under electron illumination although one would expect a decrease of these values under irradiation conditions.

Figure 6: a) Multi-diode equivalent circuit for a single NW containing one core/shell junction; b) Electrical elements of each subcell; c) Schematic of the NWs overlapping the equivalent circuit.

To reproduce the experimental conditions described in the previous section, the n-contact was placed on the top.

Figure 7: I-V characteristics in the dark (a) and under electron irradiation (b): dots indicate the experimental values and the continuous line indicates the numerical simulation; c) Experimental and d) simulated EBIC profile along the NW axis at -1.5 V.

These indications point out that the resistance extracted from the fit is not representative of the NW, but of the other elements of the electrical system. We suppose that this discrepancy arises from the high value of the contact resistance at the tungsten tip/NW interface due to the small radius of the manipulator tip used for the measurement.

The analysis of the contact resistance is challenging since it depends on many parameters such as the surface chemistry (presence of an oxide layer) and the mechanical force exercised by the manipulator on the NW, which depends on the NW flexibility^{44,45}. Although the exact values obtained for the core and the shell may be questionable, the ratio between R_{core} and R_{shell} is characteristic of the measured NW. Indeed, the slope of the EBIC profile is very sensitive to the relative variation of these two resistances: a difference between the resistance values leads to a decrease of the current along the length of the NW²².

A good fitting of the experimental EBIC profile can be achieved only taking well balanced core and shell resistances $R_{\text{core}}=R_{\text{shell}}$.

Parameters	I-V (dark)	I-V (under e- beam) and EBIC
I_{sat} (pA)	0.08	0.08
η	12	6.8
R_{sh} (G Ω)	$>10^3$	$>10^3$
I_{illum} (pA)	-	0.6
R_{core} (G Ω)	42.5	42.5
R_{shell} (G Ω)	42.5	42.5
R_{eff} (G Ω)	85	85

Table 1: Fitting parameters; aside, the single NW I-V characteristic in the dark, indicating the regimes where specific parameters have the strongest influence.

EBIC Analysis on the NW Array

In order to analyse the properties of macroscopic NW arrays, NW ensembles were electrically contacted. To ensure an electrical insulation between the top and bottom contacts, the NWs were encapsulated in hydrogen silsesquioxane (HSQ). The encapsulation was done by spin coating at 4000 rpm for 4 minutes and annealed at 400°C for 120 minutes. After a step of CHF_3 plasma etching to remove the residues of the spin-on glass from the NW tops, ITO was sputtered to form a top transparent contact. Circular ITO contacts with ~ 2.3 mm diameter were deposited through a shadow mask.

The morphology of the ITO-contacted NW arrays is illustrated in Figure 8a. A schematic of the processed sample is shown in Figure 8b.

Then, the sample was characterized by EBIC mapping in order to investigate the carrier generation and collection with a nanoscale resolution. After this first assessment, samples were annealed to improve the ITO contact and the EBIC analyses were repeated.

All EBIC measurements were performed using the same set-up described in the previous section.

However, due to the electron-shielding effect of the top ITO contact a more energetic beam has been used to penetrate through the ITO and probe the NWs underneath (10 kV acceleration voltage and 625 pA injected current).

Figure 8: a) Secondary electron (SE) image of the GaAs NW array protruding from the encapsulation layer. In the inset, a high magnification SE image of a single NW covered by the ITO top contact; b) Schematic of the sample after processing.

No external bias was applied. EBIC maps before annealing present both negative (black) and positive (white) electrical signals, indicating the presence of diodes with opposite orientations (Figure 9a). For the positive signal, the direction of the induced current flow is coherent with the signal of the radial junction. It is observed that the black signal is strongly localized while the white one is diffused over the whole surface, except for few NWs presenting a localized white signal. The secondary electron (SE) contrast for these anomalous NWs is lower, which likely shows that their top part was broken.

Figure 9: a) SE image and corresponding EBIC map of the NW array. The white contrast on the EBIC map corresponds to the radial junction signal while the black contrast is given by a Schottky barrier at the ITO/NWs interface. Dashed lines show the position of the profiles analyzed in panel b). Investigated NWs are labelled as α to ϵ . b) Induced current profile (black) and SE contrast (blue) are plotted with respect to the position along the dashed lines. c) Schematic of the interaction volume/NW overlap when the electron beam is positioned close to a NW.

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In order to understand the origin of the two opposite signals, line profiles were acquired from both the SE image and the EBIC map enabling the comparison of the electrical signals with the position of the NWs along the scanned surface. Results are shown in Figure 9b. For the sake of clarity, the line profile position is indicated by dashed lines in both the SE image and EBIC map, and the analyzed NWs are labelled from α to ε .

The comparison between the SE and EBIC profiles shows that the localized black signal coincides with the position of the NWs, while the diffuse white signal is progressively increasing when approaching the NWs. Since in EBIC mapping the signal is collected from an area where the interaction volume overlaps with the internal field region³⁷, the different localization of the two signals on the sample surface and the absence of any diodic element other than the NWs suggests that the electrical signals originate from the NW regions located at different depths (see illustration in Figure 9c schematically showing the interaction volume).

For a PV application perspective, it is important to analyze the positive (white) signal arising from the p-n

the NWs and its intensity is increasing when the beam approaches the NWs indicates that it originates from a larger depth from the top surface (where the interaction volume is broadened) than the black signal which, on the contrary is strongly localized on the NW position. This analysis is coherent with the attribution of the positive signal to the radial p-n junction. In turn, the presence of a Schottky barrier at the NW/ITO interface induces a band bending oriented in the opposite direction than the built-in field of the radial junction and therefore yields a negative signal. These observations show that it is crucial to optimize an ohmic top contact to avoid the parasitic Schottky diode at the NW/ITO interface.

By analyzing low magnification EBIC maps, the percentage of NWs containing an active radial junction (i.e. producing a positive EBIC signal around their periphery) has been evaluated. In different regions of the array it is estimated around $55 \pm 4.5\%$. It should be noticed that this percentage refers only to the signal collected from the radial junction; the percentage of NWs producing a negative signal from the Schottky barrier with the top contact is higher (around 80%).

junction. The fact that it is collected immediately outside

Figure 10: SE images and corresponding EBIC map before (a) and after (b) the top contact annealing; c) histograms representing the distribution of the EBIC current in the EBIC maps in (a)(black line) and in (b)(red line).

This observation suggests that some of the contacted NWs do not have an active p-n junction, which may be attributed to some fluctuations of the environment (e.g. shadowing effect⁴⁶) in a spontaneously grown NW ensemble. The presence of a Schottky barrier at the interface with the top contact is surely a limitation for the performance of the device. In order to reduce this deleterious effect, the impact of the top contact annealing on the Schottky barrier is investigated by EBIC mapping. Thermal treatment of ITO films is expected to bring a significant reduction of the resistivity and an increase of the optical transmittance (as reported for annealing in a non-oxidizing environment at $T > 300^{\circ}\text{C}$ ⁴⁷). Nevertheless, to the best of our knowledge, its consequence on the GaAs/ITO interface has never been investigated with nanoscale techniques.

The sample was annealed at 400°C for 10 minutes under Ar/H_2 flux in a rapid thermal annealing oven. EBIC measurements were performed on the same sample before and after annealing; to have comparable results, the same electron beam conditions (10 kV acceleration voltage and 625 pA injected current) were used in the two cases. No external bias was applied. Results are displayed in Figure 10.

As previously discussed, before annealing (Figure 10a) the signal of the Schottky barrier is dominant on the scanned surface. Before annealing, the current averaged on the scanned area is around -16 nA, the current variation corresponding to the p-n junction is in the order of a few nA.

After annealing (Figure 10b) the average current becomes -0.14 nA, indicating a strong improvement of the electrical properties of the GaAs/ITO interface. This effect can be ascribed to a reduction of the work-function of the ITO films due to the annealing in non-oxidizing environment⁴⁸.

The overall effect of the thermal treatment on the NW array is summarized by the histograms in Figure 10c where the recurrence of the measured EBIC current for each pixel of the map is plotted together with the average current before and after annealing. By comparing the histograms obtained before and after annealing (respectively black and red curves), we can see that the current generated at the Schottky barrier is lower in

absolute value (changed from -20 nA to -6 nA at the peak). Moreover, the signal associated with the p-n junction is strongly enhanced in intensity and distribution on the area. In fact, it is possible to observe that before annealing the current generated by the p-n junction is peaked at -8.8 nA. This negative value indicates that the Schottky barrier not only impedes the collection of the carriers generated from the junction, but that generated carriers at the Schottky contact are predominant. After annealing, this peak is shifted to 10.6 nA, indicating that the current produced by the p-n junction is dominant with respect to the parasitic Schottky current. It is possible to notice also that the relative height of the peaks is largely different before and after annealing, indicating the increased spreading of the current generated in the p-n junction over the scanned surface.

Conclusions

In this work, p-n core/shell GaAs NWs were analyzed in view of their potential use as a top cell in a tandem III-V/Si solar cell. Self-assembled Ga-catalyzed NWs were grown by MBE directly on Si substrate. TEM analyses show that the GaAs NWs are mainly constituted by a ZB structure with some stacking-faults, and that the core is homogeneously covered by $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}$ double passivating shells. I-V measurements and electron beam induced current mapping of single NWs have shown the absence of the leakage current under reverse bias. The homogenous collection of carriers from the entire core length lead to an estimation of the junction area around 38 times higher than the NW footprint. Both results are favorable for application of these core/shell NWs in photovoltaic devices. The electrical parameters of the radial junction were estimated by fitting the experimental results obtained on single NWs with a numerical simulation: the results indicate that the NWs present a very low saturation current and a high shunt resistance value and that the resistance of the core and of the shell are well balanced. The properties of the NW arrays contacted by a transparent ITO contact were investigated using EBIC microscopy. EBIC maps revealed the presence of a Schottky barrier at the NW/ITO interface competing with the current induced in the p-n junction. The parasitic effect of the Schottky barrier was successfully reduced by annealing as evidenced by EBIC maps before and after the thermal treatment.

Conflicts of interest

There are no conflicts to declare.

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