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Physics and design for 20 % and 25 % efficiency nanowire array solar cells

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Abstract

Bottom-up fabricated single-junction III-V nanowire array solar cells have shown efficiency up to 15.3 %, which is approximately half of the conventional Shockley-Queisser detailed balance efficiency limit of 33.6 %. Here, based on numerical and analytical opto-electronics modeling and analysis, we give guidelines for (i) geometry that gives strong absorption as well as (ii) the design of efficient p-n junction and electrical contacts in the nanowires to reach 20 % and 25 % efficiency. We exemplify the impact of 8 different optical and electrical loss mechanisms in a 15 % and a 25 % design. We also provide an analytical equation for estimating the efficiency drop due to resistive losses in the top contact layer for varying cell size.

1. Introduction

The solar cell market is growing exponentially, supplying approximately 1.5 % of the world electricity demand in 2016 [1]. Any improvement in solar cell materials and designs could hence have a large impact on the society. Currently, the dominating material for solar cells is Si, with demonstrated cell efficiency of 26.0 % for a single-junction cell [2]. The highest efficiency for single-junction cells under non-concentrated sunlight is 28.8 % for the III-V semiconductor GaAs [2]. However, Ga, like In, the other popular group III material in III-V solar cells, is expensive and far less-abundant in the earth's crust than Si.

Therefore, directions to reduce the cost of III-V solar cells are sought for. Bottom-up synthesis of nanowires allows the fabrication of nanowires on heavily lattice-mismatched substrates, like Si [3], which could reduce the fabrication cost of the III-V materials compared to conventional fabrication on lattice-matched, expensive III-V substrates. Promisingly, even substrate-free fabrication of III-V nanowires has been shown with the aerotaxy method [4-6]. Presently, for bottom-up fabricated nanowires, the record efficiency is 15.3 % for GaAs nanowires [7] and 15.0 % for InP nanowires [8]. The record for a top-down, etched III-V nanowire array solar cell is 17.8 %, made from InP nanowires [9].

A binary material system like InP or GaAs is expected to be easier to develop and optimize than a ternary like GaInP or GaAsP, since binaries don't show similar compositional fluctuations as ternaries. Therefore, we see large motivation in demonstrating higher efficiency with the binary III-V nanowire array solar cells. A high efficiency InP or GaAs nanowire array solar cell could be directly used as a single-junction cell that could also be made flexible. In addition, the demonstration of higher efficiency in InP or GaAs nanowire array solar cells could motivate further efforts towards tandem solar cells where a higher bandgap ternary III-V nanowire array is used as the top cell, for example on top of a Si bottom cell [10-12], as has been done already with planar III-V cells to boost the efficiency beyond 30 % [2,13,14]. We see the demonstration of 20 % and subsequently 25 % single-junction efficiency as very important steps for the III-V nanowire array solar cell research field. Here, we provide guidelines for designs toward these efficiencies.

Solar cells with both radial and axial junction have been fabricated with nanowires. However, the current efficiency record for nanowire arrays with an axial junction is more than twice as high as for nanowire arrays with a radial junction [7,9,11,15]. Therefore, we focus on the axial junction in this study. Regarding materials, one of the main differences between InP and GaAs nanowires is the surface quality. GaAs nanowires need a dedicated surface passivation like a high bandgap AlGaAs shell [7,16,17]. In contrast, InP nanowires have performed well without such a dedicated epitaxial passivation scheme [8,18]. Hence, for simplicity, we focus on InP nanowires in this study.

For a solar cell, in addition to the efficiency η of converting sunlight to electrical energy, three other parameters are usually highlighted: (1) the short-circuit current (density) j_{sc} that is extracted from the solar cell at zero external voltage bias, (2) the open-circuit voltage V_{oc} which is the maximum bias the solar cell can provide, in which case no current is extracted, and (3) the fill-factor FF that is defined through $\eta = j_{sc}V_{oc}FF/I_{inc}$ with I_{inc} the incident intensity of the sunlight.

Here, based on opto-electronics modeling and analysis, we discuss which limitations need to be overcome both on the optical and electrical side to reach an efficiency of 25 %. We focus on three aspects: (1) The optical response that dictates the limit on j_{sc} through the absorption of sunlight in the nanowires. This absorption is limited by reflection and transmission losses, as well as parasitic absorption in the transparent conductive oxide (TCO) top contact layer. (2) The electrical characteristics of the p-n junction in the nanowires. The p-n junction design affects how well photogenerated electron hole pairs can contribute to j_{sc} . The p-n junction design also affects the recombination within the nanowire at forward bias, which determines V_{oc} and FF . (3) The resistive losses in the TCO top contact layer, which depend on the sheet resistance of the TCO layer as well as the cell size.

We consider two geometries in more detail: We start from 1500 nm long InP nanowires in a hexagonal array with 500 nm pitch, which were used in recent experiments [8]. With our modeling framework, we predict for these wires an efficiency of 14.8 %. For the second system, we increase the length of the nanowires to 3000 nm and pack them slightly denser at a pitch of 440 nm. In this way, due to enhanced absorption, the j_{sc} potential is increased by 15 %. If at the same time, the materials quality is improved and the p-n junction and contact design are optimized, we predict an efficiency of 25 %. Finally, we provide an analytical equation for estimating the efficiency drop due to resistive losses in the top contact layer for varying cell size.

2. Nanowire array geometry

We assume that the sunlight is incident at normal angle to the nanowire array solar cell, that is, parallel to the axis of the nanowires. This incidence direction maximizes the projected area of the solar cell to the incident light, giving the prospect of highest output power, when absorption and consecutive extraction of the photogenerated carriers is optimized. We assume a terrestrial solar cell at a temperature $T = 300$ K throughout.

Figure 1. (a) Schematic of InP nanowires of diameter D and length L in a hexagonal array of pitch P , which is the center-to-center distance between nearest-neighbor nanowires. The array is on top of an InP substrate and there is a planarized polymer of refractive index $n = 1.5$ between the nanowires. Here, we indicate in the right-most nanowire the axial p-i-n junction configuration. (b) The same as (a) but now with TCO top contact layer of thickness t_{TCO} on top of the nanowire array and an ARC layer of thickness t_{ARC} on top of the TCO layer.

Many previous studies have considered a square array of nanowires [19-21]. Here, we choose to consider a hexagonal array (Figure 1) since there, the nanowire surface coverage is 15 % higher for given pitch P , which is beneficial for absorption of light if P is fixed between the square and hexagonal array (Supplementary Information Figure S1). Also, if performing alignment (see Figure 11 in Ref. [12]),

of for example aerotaxy wires [4], the nanowires form such a close-packed hexagonal array. When considering the square and hexagonal array for a given nanowire length L , and using optimum pitch and nanowire diameter D , the resulting j_{sc} for the two array types is within 0.2 % and the nanowire surface coverage is within 5 % (see Supplementary Information Figure S1). A similar, rather weak dependency on the array symmetry has been discussed in terms of selected absorption spectra [15].

To planarize the array, we assume a polymer between the wires. Regarding the electrical properties, we use the substrate as the back contact and a TCO layer of thickness t_{TCO} at the top as the front contact, with accompanying anti-reflection coating (ARC) of thickness t_{ARC} (Figure 1b).

Table 1. Parameters central to the study.

<p><u>Geometry</u></p> <p>D – diameter of nanowires</p> <p>L – length of nanowires</p> <p>P – pitch of nanowire array</p> <p>t_{TCO} – thickness of TCO layer</p> <p>t_{ARC} – thickness of ARC layer</p>
<p><u>Materials</u></p> <p>n – refractive index</p> <p>E_{bg} – bandgap</p> <p>τ – effective lifetime of minority carriers</p> <p>N_D – donor concentration in top n-segment</p> <p>N_A – acceptor concentration in bottom p-segment</p> <p>N_{mid} – acceptor concentration in middle p-segment</p> <p>$L_{D,e/h}$ – diffusion length of electrons/holes</p>
<p><u>Solar cell parameters</u></p> <p>η – efficiency of solar cell</p> <p>V_{oc} – open-circuit voltage</p> <p>j_{sc} – short-circuit current</p> <p>FF – fill factor</p> <p>$j_{sc,opt}$ – limit on j_{sc} from absorption</p> <p>$j_{sc,max}$ – maximum j_{sc} for InP (35.0 mA/cm²)</p>

3. Results

In section 3.1, we consider the absorption in the nanowires, first without and then with the TCO layer. In this way, we optimize the geometry for absorption of incident light in the nanowires. In section 3.2, we turn into considering the p-n or p-i-n junction within the nanowire. First, we consider how the

junction design affects the collection of photogenerated carriers to short-circuit current. After that, we study how the junction design affects the open-circuit voltage and fill-factor, and finally the efficiency of the nanowire array solar cell. In section 3.3, we summarize the optical losses and the losses in the p-n or p-i-n junction in the nanowires, with special focus on a 15 % and 25 % efficient cell. In section 3.4, we derive analytical equations for how the size of the cell and the sheet resistance in the TCO top contact layer affects the efficiency. To aid the reader, we list in Table 1 central parameters used in the study.

3.1 Optical considerations

III-V nanowire arrays show strong diffraction of light, in which case the regular Beer-Lambert law of bulk absorption does not apply [19-23]. Through measurements, it was shown that a nanowire array can absorb almost all the incident light, even if the nanowires cover only 10 % of the surface [24].

Therefore, a lot of research focus has been on understanding and optimizing the interaction of light with nanowire arrays. By comparing measured and modeled spectra, it was shown that electromagnetic optics, using the refractive index of the bulk material of the nanowires, gives very accurate description of the optical response of nanowire arrays [25]. In that case, diffractive effects are considered in the modeling through the Maxwell equations. Also here, for accurate results, we use such optics modeling [26]. We use tabulated values for the refractive index of InP [27], and for the TCO, we use the values shown in the Supplementary Information Figure S3 of Ref. [18]. For the polymer between the nanowires, we assume a typical value of $n = 1.5$.

Since the hexagonal array is not symmetric for 90° rotation around the axis of a nanowire, to represent unpolarized sunlight, we model twice for each wavelength and average the results: once with x-polarized and once with y-polarized incident light, where x is a direction in which nearest-neighbor nanowires are separated by P . However, the maximum difference in j_{sc} calculated separately for x and y polarized light is only 1 % for the arrays considered in this study. Thus, the hexagonal array does not cause a strongly polarized broadband response.

As useful absorption, we consider only absorption in the nanowires. In other words, we consider the transmission of light into the substrate as a loss, even if photogeneration of electron-hole pairs occurs also in the substrate. That is, we assume that the probability for photogenerated carriers from the substrate to contribute to the short-circuit current is negligible – the motivation for this assumption is based on measured electron-beam induced current (EBIC) profiles, as discussed in more detail in Section 3.2.1.

3.1.1 Optimized absorption of sunlight

We start by considering the bare nanowire array with the $n = 1.5$ polymer between the nanowires (see Figure 1(a)). In Section 3.1.3, we include the TCO top contact layer and the ARC on top of it (see Figure 1(b)).

In nanowire arrays, distinct optical modes show up [19,28,29]. For solar cell operation with direct bandgap III-V nanowire arrays, the so-called HE_{1m} modes are singled out as very important [29]. Each of the HE_{1m} modes can cause a distinct absorption peak. The position of the peak in the absorption spectrum can be tuned with the nanowire diameter – by increasing the diameter, the absorption peak red-shifts. The HE_{11} mode is the fundamental mode, which shows an absorption peak at the longest wavelength, or equivalently, for a given wavelength at the smallest diameter [29].

Previously, it was shown that an optimum way to choose the diameter is to choose it such that an HE_{1m} mode gives an absorption peak close to the bandgap wavelength [29]. In this case, the absorption through the peak of the HE_{1m} mode enhances absorption in the region just above the bandgap in energy where the absorption coefficient of the semiconductor is typically low. Then, for fixed nanowire length L , the array pitch P is tuned to enhance absorption at shorter wavelengths [29].

First, we consider an array with $D = 180$ nm, $P = 500$ nm, and $L = 1500$ nm, which was the geometry in recent EBIC experiments aimed toward higher efficiency nanowire array solar cells [8]. Here, for comparison and demonstration of the strong optical tunability, we show results also for $D = 120$ nm and $P = 333$ nm, as well as for $D = 270$ nm and $P = 750$ nm (Figure 2(a)). Note that these two arrays contain the same amount of absorbing material as the array with $D = 180$ nm and $P = 500$ nm, since the D/p ratio is fixed and all have the same L .

For $D = 180$ nm, we see an absorption peak at $\lambda \approx 820$ nm, which is due to efficient coupling of incident light into the HE_{11} mode and strong absorption of the HE_{11} mode at this wavelength [29]. In this way, the absorption is rather strong for the whole spectral range, except for a dip in the intermediate $500 < \lambda < 750$ nm range. In contrast, for $D = 120$ nm, the HE_{11} mode shows a blue-shifted peak at $\lambda \approx 600$ nm. The longer wavelengths are absorbed poorly due to the onset of the electrostatic screening, which shows up for small D/λ where light is not efficiently coupled into the nanowires [23]. For $D = 270$ nm, the HE_{11} absorption peak has red-shifted to the non-absorbing region beyond the bandgap wavelength, and the HE_{12} absorption peak is at $\lambda \approx 600$ nm. Except for this $\lambda \approx 600$ nm region, this array with the highest pitch shows weaker absorption than the two other arrays considered.

Next, we consider the effect of the nanowire length at the optimum diameter of $D = 180$ nm (Figure 2(b)). For short nanowires, the HE_{11} absorption peak at $\lambda \approx 820$ nm is clearly seen. With increasing

nanowire length, the absorption starts to saturate, and for $L > 2500$ nm, the absorption looks rather saturated for $\lambda < 900$ nm, that is, for almost the whole wavelength region below the bandgap wavelength of InP of 925 nm.

The absorption saturates at values of about 93 %, limited by the reflection R_{top} at the top interface of the array (dashed line in Figure 2(b)) [20,24,29]. From the Fresnel equations for normally incident light, such a 7 % reflection would occur for a planar interface between air and a material with refractive index $n \approx 1.70$ -1.75. Actually, by geometric averaging of the refractive index of the InP (≈ 3.5 for $\lambda > 500$ nm) and the $n = 1.5$ polymer, we obtain in good agreement the value $n_{\text{geom}} = 3.5\pi \left(\frac{D}{2}\right)^2 / \sqrt{\frac{3P^2}{2}} + 1.5 \left(\frac{\sqrt{3}P^2}{2} - \pi \left(\frac{D}{2}\right)^2\right) / \sqrt{\frac{3P^2}{2}} \approx 1.74$.

In summary, by increasing the nanowire length, we end up in a case where the absorption is limited just by the reflection loss at the top side, which occurs before the light enters the nanowire array.

Figure 2. (a) The absorption in an array of nanowires of $L = 1500$ nm in length at a constant diameter to pitch ratio, D/P . See Figure 1(a) for schematic. (b) Same as (a) but for varying nanowire length at fixed $D = 180$ nm and $P = 500$ nm.

3.1.2. Absorption in terms of short-circuit current

Next, we focus on the optimum $D = 180$ nm and the capacity of the nanowires to photogenerate electron-hole pairs (Figure 3). Here, the absorption for $270 < \lambda < 925$ nm in wavelength is of interest: The AM1.5G spectrum that we consider shows negligible intensity for $\lambda < 270$ nm = λ_{short} [30], and we assume no contribution from photons with wavelength beyond the bandgap wavelength of $\lambda_{\text{bg}} = 925$ nm of InP. In this case, we obtain the upper limit, as set by the absorption, for the short-circuit current as [31,32]:

$$j_{sc,opt} = q \int_{\lambda_{short}}^{\lambda_{bg}} \frac{I_{AM1.5}(\lambda) A_{inc}(\lambda)}{2\pi\hbar c/\lambda} d\lambda \quad (1)$$

where q is the elementary charge, $\hbar$ the reduced Planck constant and c the speed of light in vacuum, $I_{AM1.5}(\lambda)$ the AM1.5G incident solar spectrum [30], and $A_{inc}(\lambda)$ the absorption in the nanowires (see Figure 2 for examples of $A_{inc}(\lambda)$). Here, we assume that each photon absorbed in the nanowires contributes one charge carrier to the short-circuit current. That is, we assume perfect collection efficiency of the photogenerated electron-hole pairs in the nanowires. As a reference value, we use the maximum $j_{sc,opt}$ of $j_{sc,max} = 35.0 \text{ mA/cm}^2$ for InP, which occurs when $A_{inc}(\lambda) = 1$ for $\lambda_{short} < \lambda < \lambda_{bg}$ in Eq. (1).

Figure 3. (a) Short-circuit current potential $j_{sc,opt}$ of the nanowire array in Figure 1(a) for varying nanowire length L and array pitch P at the optimum nanowire diameter $D = 180 \text{ nm}$. (b) Maximum $j_{sc,opt}$ from (a) for varying L . The inset shows the pitch at which this $j_{sc,opt}$ is reached.

First, also here we see the effect of the top-insertion reflection loss. This top-insertion reflection gives the upper limit on the short-circuit current, corresponding to absorption of all above bandgap photons that couple into an array of infinitely long nanowires (the dashed line in Figure 3(a)). With increasing pitch, since $D = 180 \text{ nm}$ is fixed, the insertion reflection loss decreases, going toward the 4 % loss given by the interface between air and the $n = 1.5$ polymer.

Regarding the length and pitch of the wires: A small pitch typically leads to stronger absorption of the light that couples into the array, but also to larger top-insertion reflection loss. In contrast, a larger nanowire length leads to stronger absorption that can allow for larger pitch, which decreases the top-insertion reflection loss more than it decreases the absorption in the nanowires. Therefore, with increasing length of the wires, the optimum pitch increases (see inset in Figure 3(b)).

In principle – with increasing L , since the D/P ratio goes toward zero for the optimum geometry, the $j_{sc,opt}$ would be limited just by the 4 % insertion reflection loss. Then, $j_{sc,opt}$ will go toward 96 % of $j_{sc,max}$. However, a longer nanowire will put a harder requirement on the electrical quality of the nanowire material to be able to collect the photogenerated carriers into short-circuit current, and there is for a given materials quality an upper limit on suitable nanowire length [33].

The top insertion loss can in principle be reduced with ARCs. Hence, it is the difference between the top-insertion limited $j_{sc,opt}$ (dashed line in Figure 3(a)) and the $j_{sc,opt}$ that is modeled with finite L , which indicates more fairly the loss in j_{sc} potential due to non-complete absorption in the nanowires. We see that for $L = 1500$ nm and $P = 500$ nm, we lose additional 4.9 mA/cm² beyond the top-insertion reflection loss. In contrast, for $L = 3000$ nm, at the optimized pitch of $P = 440$ nm, the additional loss is only 0.7 mA/cm². Regarding the modeled absorption in the nanowires, we find $j_{sc,opt} = 27.9$ mA/cm² for $L = 1500$ nm and $P = 500$ nm, and for $L = 3000$ and $P = 440$ nm, $j_{sc,opt} = 31.8$ mA/cm² – to be put in relation to the $j_{sc,max} = 35.0$ mA/cm² of InP.

Also, for $L > 3000$ nm, the increase in $j_{sc,opt}$ with increasing L is rather slow. We find an increase by 0.4 mA/cm² when increasing from $L = 3000$ nm to $L = 4000$ nm, when using optimum pitch for both (see Figure 3(b)). Therefore, to consider a relatively absorption-optimized system, we focus on $L = 3000$ nm and $P = 440$ nm. At the same time, we include results also for $L = 1500$ nm and $P = 500$ nm, which was used in recent experiments [8]. Then, we see how far the efficiency of that geometry could be pushed if the electrical properties are further optimized.

3.1.3. TCO top contact and ARC

In an axial junction nanowire solar cell, we need to have an electrical top contact layer, for which typically a TCO is used [7-9,18]. The TCO has two main effects on the solar cell performance: (1) The TCO leads to a certain degree of parasitic absorption of incident light. (2) The TCO leads to a resistive loss which can decrease the FF . A thicker TCO leads to less of resistive losses but to more of parasitic absorption. Hence, in principle, the TCO should be optimized for balancing the resistive loss and the parasitic absorption. Such optimization is beyond the scope of this work since the optical and electrical properties of TCOs typically depend on its exact deposition conditions. Instead, here, we study the effect of the parasitic absorption and in Section 3.4 the effect of the resistive losses on the expected performance of the solar cell. For simplicity, we assume a planar TCO (see Figure 1(b) for a schematic), even if it has been shown that nanophotonic effects from a non-planar TCO layer can in some cases boost absorption in nanowires [9,15].

Figure 4. Absorption in nanowires (NWs), absorption in TCO, reflection (R), and transmission into substrate (T), translated to corresponding short-circuit current values with Eq. (1). The nanowire diameter is $D = 180$ nm. For $L = 1500$ nm, the pitch is $P = 500$ nm, and for $L = 3000$ nm, $P = 440$ nm. See Figure 1(b) for a schematic of the array geometry.

Figure 4 shows the effect of TCO thickness on $j_{sc,opt}$. Here, we included a 100 nm thick $n = 1.5$ ARC layer at the top, a thickness which gives optimized performance according to more detailed modeling.

The TCO absorption decreases the j_{sc} potential monotonously with increasing TCO thickness. For further analysis, as a balance between TCO absorption losses and resistive losses, we choose $t_{TCO} = 50$ nm. The impact of resistive losses in the TCO layer are discussed in Section 3.4. Then, at this $t_{TCO} = 50$ nm, for $L = 1500$ nm and $P = 500$ nm, we find $j_{sc,opt} = 27.9$ mA/cm². The loss constitutes of 4.7 mA/cm² due to transmission, 1.4 mA/cm² due to reflection, and 1.1 mA/cm² due to absorption in the TCO. For the case of no TCO layer, that is, for $t_{TCO} = 0$, we find 29.2 mA/cm², which is actually higher than the 27.9 mA/cm² that was obtained in the previous section, in Figure 3(a), without the 100 nm thick $n = 1.5$ ARC.

For the case of $L = 3000$ nm and $P = 440$ nm in Figure 4, $j_{sc,opt} = 33.4$ mA/cm² for $t_{TCO} = 0$, whereas it was 31.8 mA/cm² without the ARC (Figure 3(a)). For $L = 3000$ nm, $P = 440$ nm, and $t_{TCO} = 50$ nm, we find $j_{sc,opt} = 32.1$ mA/cm². There, 1.0 mA/cm² is lost to TCO absorption, 1.1 mA/cm² to reflection, and 0.7 mA/cm² to transmission. That is, 8.2 % of the j_{sc} potential is lost. In principle, with a more advanced multi-layer ARC or nanostructured ARC, we could expect the reflection loss to go toward zero. In that case, we expect to reach 95 % of $j_{sc,max}$, where 3 percentage point of the remaining loss would be due to TCO absorption and 2 percentage point due to transmission.

3.1.4. Photogeneration profile

The above $j_{sc,opt}$ is calculated from the optical absorption and corresponds to the case of 100 % contribution to the j_{sc} of each photogenerated electron-hole pair in the nanowire. In reality, the probability that a photogenerated electron-hole pair contributes to the current is strongly dependent on the axial position in an axial p-n junction nanowire, as seen from axially-dependent, measured EBIC profiles [7,8,34].

Therefore, we calculated the axial dependence of the photogeneration by integrating over the cross-section of the nanowire at each axial position (see Supplementary Information Figure S2). Such an axially dependent photogeneration profile is used in the electrical drift-diffusion modeling in Section 3.2, and we included the above TCO with $t_{TCO} = 50$ nm and the ARC with $t_{ARC} = 100$ nm in the optics modeling. We show in Figure 5 the photogeneration rate, in terms of cumulative photogeneration translated to j_{sc} potential. We show results both for the array with $L = 1500$ nm and $P = 500$ nm; as well as for the more absorption-optimized array with $L=3000$ nm and $P = 440$ nm array.

Figure 5. Photogeneration rate in the nanowires integrated over the cross-section and translated into cumulative, axially dependent short-circuit current (see Figure S2 for the underlying photogeneration rate for $L = 3000$ nm).

For $L = 3000$ nm, we find from Figure 5 that 21.2 mA/cm² is photogenerated in the topmost 500 nm of the nanowires, with approximately 5 mA/cm² photogenerated per 100 nm of nanowire length in the topmost 300 nm. In contrast, the photogeneration in the next 5 segments of 500 nm in length is 5.9, 2.6, 1.4, 0.8, and 0.5 mA/cm² to sum up to the $j_{sc,opt} = 32.1$ mA/cm² of Section 3.1.3 for the whole nanowire. For $L = 1500$ nm, 17.7 mA/cm² is photogenerated in the topmost 500 nm of the nanowire, 6.6 mA/cm² in the next 500 nm long segment, and 3.7 mA/cm² in the bottom-most 500 nm long segment. For both $L = 1500$ nm and $L = 3000$ nm, the photogeneration in the topmost 300 nm of the

nanowire is approximately equal to that below this topmost 300 nm. Thus, efficient collection of photogenerated carriers in the topmost 300 nm is crucial for reaching high j_{sc} values.

3.2. Electrical considerations for the nanowire diode

Here, we assume that the cell size is small enough so that we can neglect resistive losses in the top TCO contact layer – such resistive losses are discussed in more detail in Section 3.4. We focus on the p-n junction diode within the nanowires and perform drift-diffusion modeling for the electrons and holes [33,35]. Such modeling gives accurate description of the electrical response of bulk-like semiconductor devices at room temperature [36]. Note that the diameter of the InP nanowires in this work is 180 nm. At such a diameter, quantization effects are negligible, and a bulk-like description of the electrons and holes in the nanowires is expected to be accurate.

For InP, unless otherwise explicitly stated, we use for the effective density of states in the conduction and valence band $N_c = 5.7 \times 10^{17} \text{ cm}^{-3}$ and $N_v = 1.1 \times 10^{19} \text{ cm}^{-3}$, for electron and hole mobility $\mu_e = 5400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, for bandgap the value $E_{bg} = 1.34 \text{ eV}$, and for the dielectric function $\epsilon = 12.25\epsilon_0$ with ϵ_0 the permittivity of vacuum [35].

Previously, we showed that axial nanowire solar cells can be analyzed with 1D modeling along the axial direction [33]. In that modeling, the electron and hole behavior in the cross-section is taken into account effectively. The photogeneration rate at a given axial position is integrated over the cross-section (see Figure 5 and Figure S2). Importantly, in that case, surface recombination at the circumference of the nanowire can be taken into account as effective bulk recombination. In the limit of weak surface recombination, the recombination lifetime of minority carriers set by surface recombination is given by $\tau_{surf} = D/(4v_{sr})$ with v_{sr} the surface recombination velocity. For the $D = 180 \text{ nm}$ wires we consider here, this expression was shown to be valid actually down to $\tau_{surf} = 45 \text{ ps}$, which corresponds to up to $v_{sr} = 10^5 \text{ cm/s}$ [33].

For the nanowire, typically, we include Shockley-Read-Hall (SRH) type surface and bulk non-radiative recombination, radiative recombination, and Auger recombination [33]. These processes have corresponding minority carrier lifetimes τ_{surf} , τ_{bulk} , τ_{rad} , and τ_{Aug} . Then, the resulting minority carrier lifetime is given by $1/\tau = 1/\tau_{surf} + 1/\tau_{bulk} + 1/\tau_{rad} + 1/\tau_{Aug}$.

Regarding Auger recombination, the corresponding minority carrier lifetime is given by $\tau_{Aug} = 1/(C \times N^2)$ with C the Auger recombination coefficient and N the doping concentration. With the previously used $C = 9 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ for both electrons and holes in InP [35], we find for $N = 10^{18} \text{ cm}^{-3}$ that $\tau_{Aug} = 1 \text{ } \mu\text{s}$ and decreases by two orders of magnitude for each increase by an order of magnitude in N . Regarding the optical recombination, the corresponding minority carrier lifetime is given by $\tau_{rad} = 1/(B \times N)$ with B

the coefficient for radiative recombination. With the $B = 1.2 \times 10^{-10} \text{ cm}^3/\text{s}$ of intrinsic InP [35], we find that $\tau_{\text{rad}} = 8 \text{ ns}$ for $N = 10^{18} \text{ cm}^{-3}$, and τ_{rad} decreases by an order of magnitude for each increase by an order of magnitude in N . Hence, when working in the range $N \leq 10^{18} \text{ cm}^{-3}$ and $\tau < 10 \text{ ns}$, we assume that Auger and radiative recombination can be neglected. Then, we assume that surface and bulk SRH type recombination determine τ .

We use the same assumptions as in Ref. [33] for the SRH recombination: A single trap level that is located at the intrinsic Fermi level; and equal electron and hole capture rates that result in equal electron and hole minority carrier lifetime of τ . In this way, thanks to the accurate 1D approximation, we can use τ as the important parameter for carrier recombination, irrespective if the recombination originates from surface or bulk SRH recombination.

We perform the drift-diffusion modeling with PC1Dmod, version 6.2, a freely available 1D drift-diffusion modelling package [37]. The benefit of the 1D approximation is that we can take into account many of the well-known results from bulk p-n and p-i-n junctions.

We consider the nanowire to consist of a 100 nm long top segment and a 400 nm long bottom segment, similarly as in the recent EBIC experiments [8]. Unless explicitly stated otherwise, for the top n-segment, we choose an activated donor concentration of $N_D = 10^{18} \text{ cm}^{-3}$ and for the bottom p-segment an activated acceptor concentration of $N_A = 10^{18} \text{ cm}^{-3}$.

InP nanowire array solar cells have shown efficiencies of 13.8 % [18] and 15.0 % [8] in experiments. To resemble these results, we varied τ in our modeling, as well as the p-doping concentration N_{mid} in the 1000 nm long middle segment (See Supplementary Information Figure S3). For $\tau = 300 \text{ ps}$ and $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$, we find $j_{\text{sc}} = 25.0 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.763 \text{ V}$, $FF = 0.778$ and $\eta = 14.8 \%$.

First, we look at how the photogenerated carriers contribute to j_{sc} in Section 3.2.1, and in Section 3.2.2, we study how the p-n junction configuration affects V_{oc} and FF .

3.2.1 Collection of photogenerated carriers for varying nanowire diode design

In Figure 5, we showed how the photogeneration profile varies strongly within the nanowire, peaking strongly toward the top of the nanowire. Therefore, it is important to study and optimize how photogenerated carriers from different parts of the nanowire can contribute to external current.

Experimentally, EBIC measurements give information about the spatial dependence of the probability for a photogenerated electron-hole pair to contribute to j_{sc} . The EBIC signal typically drops toward the top and the bottom of the nanowire [7,8]. The drop toward the top can be understood as recombination of photogenerated minority carriers at the top contact [7,35]. The drop toward the

bottom indicates similarly some kind of strong recombination site toward the bottom of the nanowires, possibly on the substrate surface. Importantly, the drop in the EBIC signal toward the bottom of the nanowire indicates that photogenerated carriers in the substrate are not expected to contribute to j_{sc} , explaining why transmission into the substrate was taken as a loss process in Section 3.1.

Therefore, we assume total recombination of excess minority carriers at the contacts, resembling perfect ohmic contacts. In PC1Dmod, such boundary condition is given by a high surface recombination velocity at the top and the bottom contact surface of the nanowire – we use a value of $v_{sr,top,e} = v_{sr,top,h} = v_{sr,bot,e} = v_{sr,bot,h} = 10^{12}$ cm/s there for both electrons and holes. We compare also to results with perfect carrier selective contacts, where minority carriers show negligible recombination. We realize such contacts with the choice $v_{sr,top,e} = v_{sr,bot,h} = 10^{12}$ cm/s and $v_{sr,top,h} = v_{sr,bot,e} = 1$ cm/s.

Here, we use the $\tau = 300$ ps that gave the modeled 14.8 % efficiency above, and we focus on the spatially resolved internal quantum efficiency (SIQE) [35], which shows the probability that a photogenerated electron-hole pair contributes to the short-circuit current. In Figure 6, we show the results for $N_{mid} = 10^{15}$ cm⁻³, 10^{16} cm⁻³, and 10^{18} cm⁻³ with ohmic contacts, as well as for $N_{mid} = 10^{18}$ cm⁻³ with carrier selective contacts. We have solved for the SIQE both numerically in PC1Dmod (solid lines in Figure 6) as well as fully analytically (circles in Figure 6 – see Supplementary Information for details of the analytical calculations). We find excellent agreement between the two types of solutions. Importantly, the analytical solutions allow for easier explanation of the behavior of the SIQE.

First, since $N_A = 10^{18}$ cm⁻³ in the bottom 400 nm segment and $N_D = 10^{18}$ cm⁻³ in the top 100 nm segment, the case of the p-type $N_{mid} = 10^{18}$ cm⁻³ corresponds to a pn-junction 100 nm from the top of the nanowire. For this case, we see an almost linear drop from the junction toward the contacts. To understand this linear drop, we calculated the (effective) diffusion length of the electrons and holes: $L_{D,e/h} = (D_{e/h}\tau)^{1/2}$ with $D_{e/h} = \mu_{e/h}kT/q$ the diffusion coefficient where k is the Boltzmann constant. For the $\mu_e = 5400$ cm²V⁻¹s⁻¹ and $\mu_h = 250$ cm²V⁻¹s⁻¹, we obtain for this $\tau = 300$ ps: $L_{D,e} = 2050$ nm and $L_{D,h} = 440$ nm. Thus, $L_{D,e}$ is longer than the 1400 nm bottom p-segment, and $L_{D,h}$ is longer than the 100 nm long top n-segment. In that case, to a good approximation, the photogenerated minority carriers in either region diffuse to either the pn-junction or to the respective contact, with linear dependence on the distance to the pn-junction for charge extraction. In contrast, when we replace the ohmic top and bottom contact with carrier selective contacts, we find high SIQE values through the whole nanowire. In this case, the SIQE is limited just by the recombination of photogenerated minority carriers in the n or p region before they reach the p-n junction.

Figure 6. SIQE in the $L = 1500$ nm long nanowires. The top-most 100 nm of the nanowires is n-doped with $N_D = 10^{18} \text{ cm}^{-3}$ and the bottom-most 400 nm is p-doped with $N_A = 10^{18} \text{ cm}^{-3}$. The middle 1000 nm is p-doped with N_{mid} . Note that $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$ corresponds to a 1400 nm long homogeneously p-doped bottom segment. Here, $\tau = 300$ ps and we consider either ohmic or selective contacts at the top and the bottom of the nanowire. The circles mark analytically calculated values.

For the case of ohmic contacts and $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$ and 10^{16} cm^{-3} , we find high values throughout the 1000 nm long middle segment. Thus, in contrast to the case of $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$, diffusion of photogenerated electrons from this middle segment to the bottom contact does not show up, even for the bottom-most part of the segment. These high values originate from the additional barrier for electrons to the higher p-doped 400 nm bottom segment. The increase in p-doping from 10^{16} cm^{-3} to 10^{18} cm^{-3} causes a potential barrier of 120 meV [36]. Such a barrier prohibits efficiently the photogenerated electrons from the middle region to diffuse to the bottom 400 nm region, from which they could have reached the bottom contact. Note that for $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$, the barrier is even higher, approximately 180 meV [36].

When we look at Figure 6 in more detail, we see that for $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$, $\text{SIQE} \approx 1$ in the whole middle segment, whereas for $N_{\text{mid}} = 10^{16} \text{ cm}^{-3}$, only the topmost 400 nm of this 1000 nm long middle segment shows $\text{SIQE} \approx 1$, while a drop in SIQE to 0.95 occurs toward the bottom of the segment. This difference is explained by the width of the depletion region of the p-n junction between the top 100 nm long n segment and the p-doped middle region: $W \approx (2\epsilon(N_{\text{mid}} + N_D)V_{\text{bi}}/(qN_{\text{mid}}N_D))^{1/2}$ [36]. Here, V_{bi} is the built-in potential of the diode, which for the approximation of non-degenerate doping is given by, at no external bias applied: $V_{\text{bi}} = E_{\text{bg}}/q + [\log(N_D/N_c) + \log(N_{\text{mid}}/N_v)]kT/q$. For $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$, we find $V_{\text{bi}} = 1.11$ V and $W = 1230$ nm, and for $N_{\text{mid}} = 10^{16} \text{ cm}^{-3}$, we find $V_{\text{bi}} = 1.17$ V and $W = 400$ nm. Note that due to the large difference between N_{mid} and N_D , we expect this depletion region to reside almost completely in the middle segment (in contrast for $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$, we find $W = 59$ nm, which resides equally in the top n segment and the middle p segment).

Thus, for $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$, we expect the whole 1000 nm long middle segment to be depleted. In such a depletion region, an electric field exists, which typically separates photogenerated carriers efficiently, explaining the $\text{SIQE} \approx 1$ throughout the middle segment. In contrast, for $N_{\text{mid}} = 10^{16} \text{ cm}^{-3}$, we expect such a field only for the top-most 400 nm of the middle segment. Thus, the drop to $\text{SIQE} = 0.95$ at the bottom of the middle segment is due to recombination of electrons before they reach the junction at the top-most 400 nm of the middle segment.

To summarize, we see two pathways for high SIQE and consecutively high j_{sc} : (1) high-doped top and bottom segment and a lower doped segment in-between, like with $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$ where a drift field helps in collecting the photogenerated carriers efficiently, which hence resembles a p-i-n diode, or (2) carrier selective contacts, where for long enough diffusion length, we can use simply a p-n-junction since photogenerated minority carriers will eventually diffuse to the pn-junction for collection. However, as shown in the next section, these two pathways lead to different impact on V_{oc} and FF , and hence η : A p-n junction allows for higher V_{oc} and FF .

3.2.2. Efficiency for $L = 1500 \text{ nm}$ and $P = 500 \text{ nm}$ vs $L = 3000 \text{ nm}$ and $P = 440 \text{ nm}$

Here we turn to study simultaneously j_{sc} , V_{oc} , FF , and η . We start by considering the array with $L = 1500 \text{ nm}$ and $P = 500 \text{ nm}$ for varying lifetime τ (Figure 7). We include results for ohmic contacts as well as for perfect carrier selective contacts. For the p-doping of the middle segment, we consider both $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$ and $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$, which give rise to the p-i-n and p-n diode, respectively.

First, we look at the short circuit current in Figure 7(a). With the selective contacts and increasing τ , the probability to collect photogenerated carriers, SIQE , approaches 100 % in the whole wire. Then, j_{sc} approaches the absorption limited $j_{\text{sc,opt}} = 27.9 \text{ mA/cm}^2$ of Section 3.1.3. For the ohmic contacts, there is not a very strong dependence on τ . Already at $\tau = 300 \text{ ps}$, the SIQE shows rather triangular shape for the $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$ p-n junction and trapezoidal shape for the $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$ p-i-n junction (Figure 6), and those triangular and trapezoidal shapes are the limits for $\tau \rightarrow \infty$ when contact recombination outside the depletion region gives a linear gradient in SIQE .

At small τ , the V_{oc} in Figure 7(b) is limited by recombination in the depletion region. To first approximation, the amount of recombination is then linearly dependent on the width of the depletion region and the ideality factor is 2 [36]. Then, since the width of the depletion region for $N_{\text{mid}} = 10^{15} \text{ cm}^{-3}$ is the full low-doped middle segment of 1000 nm in width, but only 60 nm for $N_{\text{mid}} = 10^{18} \text{ cm}^{-3}$, we expect a voltage boost by $\Delta V \approx \log(1000/60)2kT/q \approx 150 \text{ mV}$, in good agreement with the $\Delta V \approx 170 \text{ mV}$ found for low τ in Figure 7b.

In the pn-junction with ohmic contacts, the V_{oc} settles rather quickly with increasing τ . There, for $\tau > 1$ ns, V_{oc} is limited by contact recombination and independent of τ . In contrast, with selective contacts for the pn-junction, the V_{oc} keeps on increasing with τ . Note that in reality, there is a limit on how much the V_{oc} can increase – at some point, either radiative recombination or Auger recombination will limit further increase in τ .

Figure 7. (a) j_{sc} , (b) V_{oc} , (c) FF , and (d) efficiency η for the nanowire array with $L = 1500$ nm, $P = 500$ nm, and $D = 180$ nm as a function of lifetime τ . The nanowire array includes a 50 nm thick TCO layer at the top and 100 nm thick ARC on top of the TCO layer – see Figure 1(b) for a schematic. Here, *p-n* denotes the case of $N_{mid} = 10^{18}$ cm⁻³, in which case the 100 nm top-most part of the nanowire is n-doped with $N_D = 10^{18}$ cm⁻³ and the remaining 1400 nm is p-doped with $N_A = 10^{18}$ cm⁻³. Similarly, *p-i-n* denotes the case when the 1000 nm long segment below the 100 nm long n-doped segment is p-doped with $N_{mid} = 10^{15}$ cm⁻³. Results are shown for either ohmic or selective contacts at the top and bottom of the nanowire.

Regarding the fill factor shown in Figure 7(c), for small τ , we find a 0.05 higher FF for the p-n junction than for the p-i-n junction. This difference is higher than that obtained from the estimates of FF with varying V_{oc} [38]. Also, the FF in our simulations is lower than that in those estimates, by as much as 0.10, and FF grows rapidly with increasing τ . This lower FF , larger difference between the p-n-junction and p-i-n junction diode, and rapid increase of FF with increasing τ , we ascribe to the breaking down

of the superposition principle at small τ [33]: When the superposition principle fails, the FF drops [33]. Furthermore, we expect the superposition principle to break worse in the p-i-n junction diode that has a longer depletion region.

Importantly, it appears that it is not trivial to reach 20 % efficiency with this $L = 1500$ nm and $P = 500$ nm geometry (Figure 7(d)). Indeed, more detailed calculations with varying N_{mid} and τ showed that 20 % efficiency is not reached for $\tau < 10$ ns if ohmic contacts are used (see Supplementary Information Figure S3). However, with perfect carrier selective contacts and a p-n junction, the lifetime of 300 ps is enough to reach 20 % (Figure 7(d)). But it appears difficult to reach 25 % efficiency with $L = 1500$ nm and $P = 500$ nm, even with selective contacts. Therefore, we turn to study the more absorption optimized geometry with $L = 3000$ and $P = 440$ nm, which has the potential of 15 % higher j_{sc} compared to this $L = 1500$ nm and $P = 500$ nm.

For this more absorbing system with $L = 3000$ nm and $p = 440$ nm, we find with 1 ns lifetime, p-n junction, and ohmic contacts an efficiency of 20 % (see Supplementary information Figure S4). For 1 ns lifetime, p-n junction, and perfect carrier selective contacts, an efficiency of 25 % is reached. If the lifetime is increased to 3 ns, an efficiency of 27 % is reached.

3.2.3. Analytical calculation of V_{oc} for contact-recombination limited case

In Figure 7(b), with increasing lifetime, the limit for the p-n junction with ohmic contacts appears at $V_{\text{oc}} = 0.925$ V. This limit originates from electrically injected minority carriers at forward bias, which diffuse to the top and/or the bottom contact and recombine there. We can solve analytically for this injection, diffusion, and recombination. In that way, we obtain enhanced understanding of how the contact recombination limits the V_{oc} .

First, if we focus at the p-side: $n_{p0}p_{p0} = N_cN_v\exp(-E_{\text{bg},p}/kT)$ with bandgap $E_{\text{bg},p}$ on the p-side [36]. Here, $p_{p0} = N_A$ and n_{p0} are the equilibrium hole and electron concentrations. Then, $n_{p0} = \frac{N_cN_v}{p_{p0}}\exp\left(-\frac{E_{\text{bg},p}}{kT}\right) = \frac{N_cN_v}{N_A}\exp\left(-\frac{E_{\text{bg},p}}{kT}\right)$. The diffusion of electrons on the p side gives rise to the current [36]:

$$j_{\text{diff},p} = qD_e \frac{dn}{dz}. \quad (2)$$

If we assume that the bottom contact is at $z = 0$ and the end of the region over which carriers need to diffuse to reach the contact is at $z = W_{\text{bot}}$, then we have the conditions $n(z = 0) = n_{p0}$ and $n(z = W_{\text{bot}}) = n_{p0}(\exp(qV/kT) - 1) + n_{p0}$. That is, electrons are injected at the top side of the

bottom region over the pn-junction at the voltage V – that is, we assume that the lifetime is long enough that voltage drop does not occur over the depletion region (or more properly, drop in the electron quasi-Fermi level does not occur [36]).

Furthermore, if we assume that the lifetime is long enough such that recombination in the region of width W_{bot} is negligible, then the current in the region is constant. In this case, we find as solution: $n(z) = n_{p0}[\exp(V/kT) - 1]z/W_{\text{bot}} + n_{p0}$. From this expression we can calculate with Eq. (2) the current due to electron diffusion to the bottom contact:

$$j_{\text{contact,bot}} = \mu_e kT \frac{N_c N_v}{W_{\text{bot}} N_A} e^{-\frac{E_{\text{bg,p}}}{kT}} (e^{qV/kT} - 1) A_{\text{area-coverage}} \quad (3)$$

where, to take into account that current flows only through the cross-section of the nanowires, $A_{\text{area-coverage}}$ is the fraction of surface area covered by nanowires, which is $\pi(D/2)^2/(P^2\sqrt{3}/2)$ for the hexagonal array.

Similarly, we obtain for the diffusion to the top contact over a top region of width W_{top} :

$$j_{\text{contact,top}} = \mu_h kT \frac{N_c N_v}{W_{\text{top}} N_D} e^{-\frac{E_{\text{bg,n}}}{kT}} (e^{qV/kT} - 1) A_{\text{area-coverage}} \quad (4)$$

where we allow for different bandgap in the top and bottom segment, but, for simplicity, we assumed the same N_c and N_v in the top and bottom region.

By noting that $j_{\text{sc}} = 19.5 \text{ mA/cm}^2$ for the p-n junction system in Figure 7(a) at large τ , we solved from Eq. (3) and Eq. (4) for a limiting V_{oc} by $j_{\text{contact,bot}} + j_{\text{contact,top}} = j_{\text{sc}}$. This yields $V_{\text{oc}} = 0.923 \text{ V}$ in excellent agreement with the $V_{\text{oc}} = 0.925 \text{ V}$ at $\tau = 10 \text{ ns}$ in Figure 7(b). Regarding the contribution of the top and bottom segments: The top segment by itself would limit V_{oc} to 0.945 V and the bottom segment to 0.935 V. Thus even if the bottom segment is approximately 14 times longer than the top segment, it limits V_{oc} more since $\mu_e/\mu_h > 20$. (Note that in the derivations above, for analytical convenience, we assumed non-degenerate doping, even if the top n-segment is slightly degenerately doped.)

3.2.4 Pathways to carrier selective contacts and 25 % efficiency

From Eqs. (3) and (4), we see that an increase of the bandgap in the segment closest to the contact reduces the leakage to the contact exponentially. The length of the segment, that is, W_{bot} or W_{top} , affects the current linearly in the denominator, as does the doping of the segment. Furthermore, the mobility of the minority carriers affects the current linearly. In other words, since the dependence on the voltage of the leakage current is $e^{qV/kT}$, if we assume that leakage to that contact limits V_{oc} , an

increase of the bandgap increases V_{oc} linearly. There, an increase of the doping density or the segment length, or a decrease of the mobility of the minority carriers, of the segment increases V_{oc} logarithmically with the coefficient kT/q . Thus, an increase of the doping or segment length, or a decrease of the mobility, by a factor of 10 increases V_{oc} by $\log(10)kT/q \approx 60$ mV. For example, as discussed in Section 3.2.2, the bottom segment limited V_{oc} to 0.935 V when $N_A = 10^{18} \text{ cm}^{-3}$ there (Figure 7(b) – the large- τ limit of the p-n junction with ohmic contacts). If the doping was reduced to $N_A = 10^{17} \text{ cm}^{-3}$, we can immediately deduce that the contact-recombination limited V_{oc} would drop by 60 mV to 0.875 V.

In addition to the V_{oc} considerations, the above considerations apply also for diffusion of photogenerated minority carriers. In other words, the proposed increase of bandgap, increase of segment length, increase of segment doping, and decrease of the mobility of minority carriers can be used for reducing the diffusion of photogenerated minority carriers over the segment to the contact. Thus, in that way, the SIQE in the rest of the nanowire can be enhanced by reducing the leakage of photogenerated carriers to the contact.

Based on the above considerations for carrier selective contacts, we consider the $L = 3000$ nm and $P = 440$ nm, which showed 27 % efficiency at $\tau = 3$ ns in Section 3.2.2 for the p-n junction with perfect carrier selective contacts. Note that at $\tau = 3$ ns, the electron diffusion length is $L_{D,e} = 6500$ nm. Hence, we can indeed rely on diffusion for efficient extraction of photogenerated minority carriers from the 2900 nm long, p-doped bottom part of the nanowire.

For carrier selectivity at the bottom contact, we increased the band gap by 200 meV in the 400 nm bottom-most part of the nanowire to $E_{bg} = 1.54$ eV. For carrier selectivity in the top contact, we used a linear grading in n-doping from 10^{18} cm^{-3} to 10^{19} cm^{-3} , which creates also a drift-field to further aid in the collection of photogenerated carriers [35]. In this way, we reached $j_{sc} = 30.7 \text{ mA/cm}^2$, $V_{oc} = 0.990$ V, $FF = 0.849$, and $\eta = 25.8$ %. For example, without the linear grading in the n-doping in the top segment, we reach an efficiency of 24.6 % at the $\tau = 3$ ns, and an increase of τ to 5.5 ns is needed to increase η to 25.0 %.

3.3. Loss analysis for 15 % and 25 % cells

In Figure 8, we summarize the losses of the above 14.8 % and 25.8 % cells relative to the 33.6 % Shockley-Queisser detailed balance limit, which is obtained with the AM1.5G 1000 W/m^2 incident sunlight [31,32]. This Shockley-Queisser limit is obtained when assuming that all above bandgap photons contribute one electron hole-pair to the short-circuit current, giving $j_{sc} = j_{sc,max} = 35.0 \text{ mA/cm}^2$.

Regarding losses, the only loss mechanism is assumed to be emission of photons to all angles at the top side of the cell, and this yields $V_{oc} = 1.08$ V and $FF = 0.89$ [31,32].

First, for optical losses, we look at the drop in j_{sc} potential due to the sub-optimal absorption in the nanowires, caused by reflection, transmission, and the parasitic absorption in the TCO. We translate this drop to a similar relative drop in efficiency from the 33.6 % Shockley-Queisser efficiency limit. In Figure 8, these losses are termed “Reflection”, “Transmission”, and “TCO absorption”. Similarly, the loss in j_{sc} due to <100% extraction of photogenerated carriers is translated into a similar relative drop in efficiency. Here, we perform modeling first with selective top contact and then with selective bottom contact to see how much there is to gain in j_{sc} by each individual improvement. Each such relative improvement we take as a corresponding efficiency loss in the current sub-optimal system, termed “ j_{sc} loss – non-selective top” and “ j_{sc} loss – non-selective bottom”. Next, we set both the top and bottom contact to perfect carrier selective contacts to see how much the finite lifetime limits j_{sc} from the absorption-limited $j_{sc,opt}$ (note that with carrier selective contacts and $\tau \rightarrow \infty$, $j_{sc} \rightarrow j_{sc,opt}$). The corresponding relative loss in efficiency is termed “ j_{sc} loss – too low lifetime”. Similarly, for the drop in efficiency due to limited V_{oc} and FF caused by limited lifetime, we perform modeling with $\tau \rightarrow \infty$. The relative difference in V_{oc} and FF compared to the current system is then termed “ $V_{oc}\&FF$ loss – too low lifetime”. Finally, after summing all the above losses, the remaining loss compared to the Shockley-Queisser limit is assigned to a drop in V_{oc} and FF due to lack of perfect, selective contacts and termed “ $V_{oc}\&FF$ loss – non-selective contacts”.

For the above 14.8 % efficiency-design with 300 ps lifetime, the optical losses amount to 6.0 % in terms of absolute efficiency, out of which transmission losses dominate with 3.9 % (Figure 8(a)). Regarding extraction of photogenerated carriers, the loss due to lack of carrier selective contacts amounts to 2.2 % in efficiency. In this design with the long depletion region, the loss in short-circuit current due to finite lifetime amounts to just 0.2 % of efficiency. In contrast, the short lifetime causes the main efficiency loss by limiting V_{oc} and FF : a loss in efficiency of 7.1 %. On top of this, the lack of selective contacts limit the V_{oc} and FF further, causing an additional drop of 3.3 % in efficiency. Here, it is important to note that the loss in V_{oc} and FF due to non-selective contacts cannot be recovered by just including selective contacts: The V_{oc} and FF is limited at this 300 ps lifetime by recombination within the nanowire. Hence, to gain the 3.3 % due to selective contacts, the lifetime would need to be increased at the same time.

Figure 8. Varying losses in absolute efficiency for (a) the $L = 1500$ nm and $P = 500$ nm design that yields 14.8 % efficiency with ohmic contacts, $\tau = 300$ ps, $N_D = 10^{18}$ cm $^{-3}$ n-doping in the top 100 nm segment, $N_{mid} = 10^{15}$ cm $^{-3}$ p-doping in the middle 1000 nm segment, and $N_A = 10^{18}$ cm $^{-3}$ p-doping in the bottom 400 nm segment (b) the $L = 3000$ nm and $P = 440$ nm design that yields 25.8 % efficiency with $\tau = 3$ ns, linearly increasing n-doping from $N_D = 10^{18}$ cm $^{-3}$ to $N_D = 10^{19}$ cm $^{-3}$ toward the top of the top 100 nm segment, $N_A = 10^{18}$ cm $^{-3}$ p-doping in the bottom 2900 nm segment, and higher bandgap of $E_{bg} = 1.54$ eV in the bottom-most 400 nm of the bottom segment, as compared to the $E_{bg} = 1.34$ eV in the rest of the InP nanowire.

When we move to the p-n diode with the 1.54 eV bandgap bottom 400 nm segment, graded n-doping in the top-most 100 nm segment, increased lifetime to 3 ns, increased nanowire length to 3000 nm and decreased pitch to 440 nm, the efficiency shows a value of 25.8 %. When studying the different loss mechanism compared to the 14.8 % design (Figure 8(a)), we notice that all types of losses have decreased for this design, or show very small difference (Figure 8(b)). The only exception is the j_{sc} loss due to finite lifetime, which is 0.5 % for this design compared to 0.2 % for the 14.8 % design. This higher loss originates from the lack of a long depletion region in the 2900 nm long p-type bottom part of the nanowire, which results in the short-circuit current being slightly limited by the electron diffusion length. In this 25.8 % design, the optical losses amount to 2.7 %, the loss in extraction of photogenerated carriers to 1.3 %, and the loss in V_{oc} and FF to 3.9 % of absolute efficiency.

3.4. Resistive losses in top contact

When a voltage bias V_{ext} is applied in the external circuit of the solar cell in Figure 1(b), we assume that this bias applies between (i) a square metal frame at the top of the TCO and (ii) the substrate that is used as the back contact. That is, we assume that the metal frame shows a square opening of size $s_{cell} \times s_{cell}$ that defines the effective cell area. For simplicity, we assume that the substrate is so heavily doped that no voltage drop occurs in the substrate over the cell area.

However, the voltage within the cell area varies due to the resistive drop in the TCO contact layer through which the current flows to the metal frame (see Supplementary Information Figure S5). Due to this drop, the voltage in the interior of the cell is higher than exactly at the edge of the cell closest

to the metal frame. Hence, the voltage over the nanowires in the center of the cell is the highest, and these wires therefore contribute the lowest current density to the external circuit.

The nanowires feed the current $j_{NW}(x, y)$ into the top contact layer at position (x, y) . Here, $j_{NW}(x, y) = j_{NW}(V(x, y))$ is the current density of the nanowire diode. In the top contact, this current spreads within the x - y plane, and hence the continuity of current is given by

$$t_{TCO} \nabla_T \cdot \mathbf{j}_T(x, y) = j_{NW}(x, y) \quad (5)$$

where $\nabla_T = [\frac{d}{dx}, \frac{d}{dy}]$ and $\mathbf{j}_T(x, y) = [j_x(x, y), j_y(x, y)]$. We assumed that the current density in the TCO layer does not show variation in the z direction.

Next, we note that Ohm's law in the top contact layer is given by

$$\mathbf{j}_T(x, y) = -\sigma \nabla V(x, y) \quad (6)$$

where σ is the conductivity of the TCO layer. By combining Eqs. (5)-(6), we obtain:

$$j_{NW}(V(x, y)) = t_{TCO} \nabla_T \cdot \mathbf{j}_T(x, y) = -t_{TCO} \sigma \nabla^2 V(x, y) = -(1/R_{sheet}) \nabla^2 V(x, y) \quad (7)$$

where R_{sheet} is the sheet resistance of the top contact layer.

The boundary condition is given by $V(x_F, y_F) = V_{ext}$ for (x_F, y_F) at the metal frame. By solving Eq. (7) numerically, we obtain $V(x, y)$ at each V_{ext} . The IV-response of the cell can then be obtained, for example, by at each voltage value V_{ext} integrating the resulting $j_{NW}(V(x, y))$ over the cell area to give total current through the cell.

Importantly, from Eq. (7), we see that with the rescaling $x \rightarrow \alpha x = x'$, $y \rightarrow \alpha y = y'$, and $R_{sheet} \rightarrow R_{sheet}/\alpha^2 = R'_{sheet}$, the solution is the same in the primed variables. Thus, if we change the cell size s_{cell} by the factor α and R_{sheet} by the factor $1/\alpha^2$, the efficiency stays constant. Thus, from the results for varying cell size at fixed R_{sheet} , we can rescale for results for other values of R_{sheet} , or vice versa.

We used $R_{sheet} = 1000 \Omega$ for varying s_{cell} in Eq. (7), with the nanowire diode $j_{NW}(V)$ that gave 25.8 % efficiency without resistive TCO losses in Section 3.3. We found that for up to 20 % relative drop in efficiency, we could fit a second order polynomial to within 0.2 % accuracy in relative drop, resulting in relative efficiency of:

$$\eta_{rel} = 1 + 0.202(s_z \sqrt{R_{sheet}}) - 17.7(s_z \sqrt{R_{sheet}})^2. \quad (8)$$

With this simple expression, we can study how varying cell size and sheet resistance affect the efficiency. For example, at a cell size of $s_{cell} = 5$ mm, we can allow for $R_{sheet} = 90 \Omega$ before the efficiency drops below 25.0 % (3 % relative drop from the 25.8 % initial efficiency). Regarding the

choice of $t_{\text{TCO}} = 50 \text{ nm}$ for the optics analysis in Section 3.1.3: For that TCO thickness, a sheet resistance down to $300 \Omega/\square$ is predicted [39]. With that sheet resistance, a cell size of $2.5 \text{ mm} \times 2.5 \text{ mm}$ can be allowed before dropping below 25.0 %.

Furthermore, Eq. (8) works rather well also for the 14.8 % cell of Section 3.3. For example, when Eq. (8) predicts a relative efficiency of 95 %, a calculation with Eq. (7) with the actual $j_{\text{NW}}(V)$ of the 14.8 % cell gives a relative efficiency of 95.5 %. The higher relative drop with Eq. (8) can be explained by the higher j_{sc} of the 25.8 % cell that was used in deriving Eq. (8), leading to a larger resistive drop. In summary, we believe that Eq. (8) gives a good estimate of the efficiency drop due to TCO resistance, as long as the relative drop is not more than 20-30 %.

4. Discussion, outlook, and recommendations

We found 15 % efficiency for 1500 nm long nanowires at a pitch of 500 nm for a minority carrier lifetime of 300 ps. In that design, a low p-doped 1000 nm segment was depleted between a 100 nm long top n-segment and a 400 nm long higher doped bottom p-segment. Thus, we considered in practice a p-i-n diode.

One of the limiting factors of these nanowires was the sub-optimal absorption performance. Therefore, we increased their length to 3000 nm and packed them slightly more densely at a pitch of 440 nm. In terms of the potential to generate short-circuit current, the optical absorption in the nanowires goes up by 15 %.

For this more absorbing system, we find with 1 ns lifetime, and p-n junction instead of p-i-n junction, an efficiency of 20 %. When we furthermore assumed a lifetime of 3 ns and carrier selective contacts in the form of a higher bandgap bottom segment and a gradient in the doping of the top segment, we could reach 25 % efficiency. The benefit of the p-n junction relies on the shorter depletion region, which allows for a higher V_{oc} than a p-i-n junction [33]. However, there is requirement on long enough diffusion length with the p-n junction: The diffusion length of at least one type of carriers must be comparable to or longer than the nanowire length for efficient extraction of photogenerated carriers. We recommend growth of nanowire test-structures with a p-n junction at half of the nanowire length, and consecutive EBIC measurements to investigate possible potential of such nanowires for p-n junction cells. If the diffusion length is too short, then with that materials quality, we are bound to need a p-i-n junction to aid in the collection of photogenerated carriers – but that p-i-n junction comes at a cost for the V_{oc} and efficiency.

Regarding carrier selective contact: Efficient extraction of photogenerated carriers from the top of the nanowires is crucial for short-circuit current due to the very strong photogeneration in the top-most

300 nm of a typical nanowire. If planarization and exact contacting of just the top-most few tens of nanometers of each nanowire turns out tricky, then the usefulness of a doping gradient in the top segment could be limited. With variation in contact height, some wires might either not get contacted at all, or some might get contacted too far down making the doping gradient ineffective in restricting the photogenerated minority carriers from reaching the contact [33,35]. A path forward could then be a high bandgap window layer as the top segment, which reduces the photogeneration rate in the top-most part of the nanowire [33,35]. The back-side of the nanowire could be more tolerant to non-planar contacting since the photogeneration rate is typically orders of magnitude lower there compared to the top side.

On the cell level, we gave analytical equations for calculating relative efficiency drop due to the resistance of the TCO top contact (Eq. (8)). At a cell size of 5 mm, surrounded by a metal frame, we could allow a sheet resistance of $90 \, \Omega/\square$ for a 3 % relative drop, for example from 25.8 % efficiency before TCO resistive loss to 25.0 % efficiency. With simple rescaling as discussed above Eq. (8), we then find that for a cell size of 1 mm, we can allow for a sheet resistance of $5^2 \times 90 \, \Omega/\square > 2000 \, \Omega/\square$ before the efficiency drops below 25.0 %. Thus, in the demonstration of high efficiency, a small lab cell could allow for more transparent, but higher sheet-resistance, TCO. For larger cell size, the transparency of the TCO must be optimized simultaneously with the sheet resistance, as well as with contact finger design.

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