Design of Passivation Layers on Axial Junction GaAs Nanowire Solar Cells

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Abstract—We design a surface passivation scheme for axial junction GaAs nanowire solar cells and simulate its performance by coupled optical and electrical simulations. This design uses a wide bandgap AlGaAs shell layer to generate modulation doping in the active region and protect photogenerated carriers from the surface and top contact. The design has both excellent optical and electrical properties and achieves 21.3% power conversion efficiency when using realistic material parameters, which is 2.7 times higher than an optimized bare nanowire. Furthermore, the design is largely insensitive to surface quality and junction position, assuming moderate bulk material quality.

Index Terms—Device simulations, nanowires, photovoltaic cell, surface passivation.

I. INTRODUCTION

PERIODIC nanowire arrays for photovoltaic applications have received much attention in recent years for their ideal optical absorption properties [1]–[4]. Nanowires also provide natural strain relief, allowing growth on inexpensive lattice-mismatched substrates [5]–[11]. Ideally, epitaxial growth techniques might be used to grow several segments of different III–V materials along the nanowire length. The material composition in each segment would be selected to obtain the ideal combination of bandgap energies for a multijunction cell [12]–[14]. Within each segment, the doping would be switched from p-type to n-type during growth to form an axial p-n junction. Such multijunction nanowire solar cells could potentially offer extremely high efficiencies, while relieving the lattice-matching constraints associated with planar junctions.

To achieve this vision, however, potential surface effects in the nanowires require careful consideration. Many III–V compounds such as gallium arsenide (GaAs) have a large density of surface states within the electronic bandgap. These mid-gap surface states have several negative effects on photovoltaic device performance [15]–[18]. To date, experimental work has focused on the achievement of single-junction nanowire cells. Most reported works have adopted radial junctions [19]–[24] to diminish surface effects. High-performance axial-junction nanowire solar cells have only been reported by using indium phosphide (InP) [25]–[27], a material known for its surface quality [28]. For GaAs, there has been previous investigation of surface passivation strategies to reduce detrimental surface effects [18], [20], [29]–[32]. However, most of these efforts have been devoted to radial junction nanowires or uniformly doped nanowires only; little work has been done to deliberately investigate the effect of a surface passivation layer on an optimized axial p-n junction.

In this paper, we demonstrate that high-efficiency axial junctions are feasible even for a material such as GaAs with poor surface quality. Specifically, we design a passivation scheme for axial junction GaAs nanowire-array solar cells using an AlGaAs shell layer. Using coupled optical and electrical simulations, we show that our passivation design greatly improves both the short-circuit current and open-circuit voltage relative to an unpassivated nanowire device, increasing efficiency by a factor of 2.7. Our surface passivation scheme should also enhance the performance of other axial junction nanowire devices, such as photodetectors, light-emitting diodes, field effect transistors, and tunneling diodes. Importantly, an extension of this approach to nanowires containing multiple junctions could open a path toward high-efficiency multijunction nanowire cells.

II. PASSIVATION STRUCTURE DESIGN

Fig. 1(a) shows an axial-junction nanowire-array solar cell. We consider a periodic array of GaAs nanowires. Within each nanowire, an axial p-n junction is used to separate the photogenerated electron–hole pairs. Both the p-region and the n-region have exposed surfaces.

Due to the large surface-to-volume ratio of the nanowires, the surface has several negative effects on device performance. GaAs and many other III–V compounds have surface energy...
\( n_{GaAs} \) (\( N_n = 10^9 \) cm\(^{-3} \))
\( n++ GaAs \) (\( N_n = 10^9 \) cm\(^{-3} \))

**Fig. 2.** Specific passivation layer design and the doping concentration of each part.

states within the bulk bandgap. The surface states deplete the majority carriers, bending the bands so as to shift the Fermi energy toward midgap, as shown in the insets to Fig. 1(b). This effect increases the series resistance [18]. The induced field due to band bending also drives photogenerated minority carriers toward the surface, where they recombine, as shown by the arrows in Fig. 1(b). Due to these various surface effects, the efficiency of the nanowire solar cell decreases.

The goal of this paper is to passivate the surface of an axial junction nanowire solar cell with a single epitaxial layer of uniformly doped material. We choose aluminum gallium arsenide (AlGaAs) for this purpose. Fig. 2 shows our detailed design. For the core region, which is made of GaAs, we choose an intrinsic top segment and an n-type doped (\( N_D = 10^{18} \) cm\(^{-3} \)) bottom segment. The core region is covered with a 20-nm-thick p-type doped (\( N_A = 10^{18} \) cm\(^{-3} \)) \( Al_{0.8}Ga_{0.2}As \) shell. Carrier reflectors, made of 20-nm-thick heavily doped p and n GaAs (\( N_A = N_D = 10^{19} \) cm\(^{-3} \)), are placed below/above the top/bottom contacts to reduce the recombination at the contacts.

As we show below, this design has the following features. First, AlGaAs with a high aluminum mole fraction has a large bandgap, which minimizes the optical loss in the shell. Second, AlGaAs creates large barriers for both electrons and holes throughout the structure, preventing the minority carriers from being recombinated on the surface. Finally, the heterojunction between the p-type AlGaAs and the intrinsic GaAs creates a p-type modulation doping in the GaAs region. The use of an intrinsic material maximizes the minority carrier diffusion length, ensuring a large short-circuit current.

In the following sections, we use coupled electromagnetic-electronic simulations to validate this design. We first introduce the modeling methods in Section III. The optical performance of the passivation layer is discussed in Section IV. The device performance and the effects of the junction depth and surface recombination are shown in Section V. Section VI discusses the effects of the bulk lifetime on efficiency.

## III. METHODS

### A. Optical Simulation Method

We use the finite-difference time-domain method (Lumerical Solutions, Inc.) to calculate the absorption profile in the nanowire as a function of position and wavelength, denoted \( A(r, \lambda) \). The optical constants of GaAs and AlGaAs used in the simulation (refractive index and absorption length) are taken from [33]. We assume the nanowires are placed on a seminfinite GaAs substrate. The absorption spectrum \( A(\lambda) \) is found by integrating over the nanowire:

\[
A(\lambda) = \int_{GaAs} A(r, \lambda) dr. \tag{1}
\]

To obtain the carrier generation profile \( G(r) \), we weight the absorption profile by the solar spectrum and assume that each photon absorbed generates one electron–hole pair:

\[
G(r) = \int_{300 \text{ nm}}^{\lambda_s} \frac{A(r, \lambda) \lambda}{hc} I(\lambda) Sd\lambda, \tag{2}
\]

where \( \lambda_s \) is the wavelength that corresponds to the semiconductor bandgap, \( h \) is Planck’s constant, \( c \) is the speed of light in a vacuum, \( I(\lambda) \) is the AM 1.5D solar spectrum [34], and \( S \) is the area of the unit cell.

For a square array of nanowires, the absorption spectrum is independent of polarization at normal incidence. To reduce the size of the computation, we use a circularly polarized incident plane wave and approximate the generation profile as cylindrically symmetric. The generation profile is then exported to the device simulator as an excitation term.

### B. Device Simulation

We use Synopsys Sentaurus to model electrical transport in the device. The homojunction (core region) is simulated using a drift-diffusion model. The detailed simulation method for homojunctions is explained elsewhere [3]. The heterojunction between AlGaAs and GaAs is modeled using the thermionic emission model [35]. The electron and hole currents \( (J_e \text{ and } J_p) \) across the heterostructure have an exponential relation with the barrier heights \( (\Delta E_c \text{ and } \Delta E_v) \):

\[
J_n = a_n q \left[ v_{n,2} n_2 - \frac{m_{n,2}}{m_{n,1}} v_{n,1} n_1 \exp \left( \frac{\Delta E_c}{k_B T} \right) \right], \tag{3}
\]

where \( a_n \) is a dimensionless coefficient, \( v_{ni} \) is the emission velocity of the electrons (calculated using the equation \( v_{ni} \sqrt{k_B T/2\pi m_{ni}} \)), \( n \) is the electron density, and \( m_{ni} \) is the effective mass of the electrons. \( k_B \) is the Boltzmann constant, and \( T \) is the temperature set to be room temperature in the simulation. The subscripts 1 and 2 represent the materials with the lower and higher conduction band edges, respectively. A similar equation for the hole thermionic current is shown as follows:

\[
J_p = -a_p q \left[ v_{p,2} p_2 - \frac{m_{p,2}}{m_{p,1}} v_{p,1} p_1 \exp \left( -\frac{\Delta E_v}{k_B T} \right) \right]. \tag{4}
\]

We assume that the interface between AlGaAs and GaAs is perfect without any additional recombination centers. This is usually valid for the lattice-matched epitaxy of AlGaAs on GaAs [36]. Surface recombination on the AlGaAs surface is modeled by surface traps at mid gap [3]. The donor-like and acceptor-like surface states are taken to have the same densities.

The parameters used in the device simulation are listed in Table I.
TABLE I
SIMULATION PARAMETERS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Nominal values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{n}$, $\mu_{p}$</td>
<td>electron and hole mobility</td>
<td>doping dependent</td>
</tr>
<tr>
<td>$\Delta E_{c}$</td>
<td>conduction band discontinuity</td>
<td>0.315 eV [37]</td>
</tr>
<tr>
<td>$\Delta E_{v}$</td>
<td>valence band discontinuity</td>
<td>0.31 eV</td>
</tr>
<tr>
<td>$E_{g, GaAs}$, $E_{g, AlGaAs}$</td>
<td>band gap of GaAs</td>
<td>1.43 eV</td>
</tr>
<tr>
<td>$E_{p, AlGaAs}$</td>
<td>band gap of Al$<em>{0.3}$Ga$</em>{0.7}$As</td>
<td>2.1 eV</td>
</tr>
<tr>
<td>$\tau_{e}$, $\tau_{h}$</td>
<td>SRH recombination lifetimes for electrons and holes</td>
<td>1 ns except in Fig. 9</td>
</tr>
<tr>
<td>$D_{e}$, $D_{h}$</td>
<td>surface donor, acceptor like trap densities</td>
<td>$1.5 \times 10^{12}$ cm$^{-2}$</td>
</tr>
<tr>
<td>$\alpha_{n}$, $\alpha_{p}$</td>
<td>thermionic current coefficients</td>
<td>2</td>
</tr>
<tr>
<td>$m_{n, GaAs}$, $m_{p, GaAs}$</td>
<td>GaAs electron relative effective mass</td>
<td>0.067 $m_{0}$ $^a$</td>
</tr>
<tr>
<td>$m_{n, AlGaAs}$, $m_{p, AlGaAs}$</td>
<td>AlGaAs electron relative effective mass</td>
<td>0.485 $m_{0}$, 0.115 $m_{0}$</td>
</tr>
<tr>
<td>$m_{p, AlGaAs}$</td>
<td>AlGaAs hole relative effective mass</td>
<td>0.598 $m_{0}$</td>
</tr>
</tbody>
</table>

$^a m_{0} = 9.1 \times 10^{-31}$ kg is the electron mass.

Fig. 3. Maximum achievable short-circuit current of a square array of 3-μm-tall GaAs nanowires as a function of lattice constant $a$ and $d/a$ ratio.

IV. ABSORPTION PROPERTIES OF THE DESIGN

We optimize the diameter and lattice constant of the nanowire array to maximize solar absorption. Fig. 3 shows a map of the maximum achievable short-circuit current of a 3-μm-tall square array of GaAs nanowires on a semiinfinite GaAs substrate as a function of lattice constant ($a$) and diameter-to-lattice-constant ($d/a$) ratio. Only the absorption in the nanowire is considered here. The highest absorption is $\sim 25.93$ mA/cm$^2$, which is achieved with a 320-nm lattice constant and a 160-nm diameter. This is close to the perfect absorption value of GaAs (27.94 mA/cm$^2$). We, therefore, adopt these parameters in our design.

Fig. 4 shows the carrier generation rate profiles for a nanowire in the array for a bare nanowire (a) and for a nanowire with a 20-nm passivation layer (b). We observe that the two structures have similar generation profiles within the core region. The generation rate in the AlGaAs shell is lower than that in the GaAs core. Fig. 4(c) shows a magnified view of the top portion of the passivated nanowire, indicated with the red dashed box in (b). We note that there is significant absorption in the thin p++ GaAs layer below the top contact. To investigate the spectral response, we plot the absorption spectra for the bare and passivated nanowires in Fig. 5(a). Only the absorption in the core region is included. There is a large discrepancy between the two curves below 550 nm. However, the difference in absorption does not strongly affect carrier generation when the structures are illuminated by the solar spectrum. Fig. 5(b) shows the absorption of the two structures weighted by the AM1.5D photon flux density. The photon flux under the blue curve (bare nanowire) is strongly affect carrier generation when the structures are illuminated by the solar spectrum. Fig. 5(b) shows the absorption of the two structures weighted by the AM1.5D photon flux density. The photon flux under the blue curve (bare nanowire) is equivalent to a maximum current density of 25.93 mA/cm$^2$ (as shown in Fig. 3), while the one under the red curve (passivated NW) has a current density of 23.13 mA/cm$^2$.

V. CARRIER TRANSPORT IN THE DESIGN

A. Band Diagrams

We expect that the AlGaAs shell layer will form a barrier protecting both electrons and holes from reaching the nanowire surface. For Al$_{0.3}$Ga$_{0.7}$As, the commonly accepted value of the band offset at the GaAs/AlGaAs interface is approximately 0.3 eV for both the valence and conduction bands [37] (see Table I). To investigate the effect of the shell layer on carrier transport, we first plot the electrostatic band diagrams in thermal equilibrium along the dashed lines in Fig. 2. Fig. 6(a)–(d) shows the diagrams for the lines running across the intrinsic region (dashed line 1), n-region (line 2), near the top contact (line 3), and near the junction (line 4), respectively.

It can be seen from Fig. 6(a) that even though the core region (cyan) is intrinsic, the electrostatic Fermi level, shown as the dashed line, is very close to the valence band edge, indicating that the core region is effectively p-type doped. The effective doping concentration is $\sim 10^{16}$ cm$^{-3}$. This phenomenon is similar to modulation doping [38]. Because of the limited diameter of the core region (only $\sim 150$ nm), the modulation dopants in the AlGaAs shell layer (yellow) dope the whole core, instead of only creating a doped layer near the surface. By placing the dopants in the shell, rather than in the carrier transport region, the design provides p-type behavior in the core with the long-minority carrier diffusion length characteristic of an intrinsic material.
The band offset of the conduction band at the interface prevents generated minority electrons from being transported toward the surface, reducing surface recombination. Fig. 6(b) shows the band diagram of the n-region (orange), which is also covered by the p-type doped AlGaAs shell (yellow). The GaAs bands bend upward near the interface. However, due to the heavy doping of the core region, the space charge region only extends 10 nm below the interface. Most of the core region is still heavily doped and highly conductive.

Fig. 6(c) shows the band diagram below the top contact. The thin layer of AlGaAs (yellow) between the nanowire (cyan) and the top contact (blue) serves as a carrier reflector to reflect generated minority electrons, reducing recombination at the top contact. There is a smaller barrier for the majority carriers (holes) below the top contact.

Fig. 6(d) shows the band diagram near the interface between the n-type segment (orange) and the intrinsic segment (cyan). The interface is effectively a p-n junction, ensuring high open-circuit voltage.

B. J–V Response

Fig. 7(a) shows the J–V curves for an optimized bare GaAs nanowire array device (blue line) and the device with the passivation layer (red line). For the passivated NW design, both the short-circuit current and the open-circuit voltage are much higher than for the bare nanowire [see Fig. 7(a)]. The surface passivation results in a 2.7 times higher efficiency. The optimized bare nanowire design had a top-n/bottom-p structure with $10^{17}$ cm$^{-3}$ doping concentrations for both n and p regions. The junction depth was optimized with respect to power conversion efficiency, as shown in Fig. 7(b). For the bare nanowire, the optimal junction depth is very close to the top surface at ~220 nm, close to the generation hot spot shown in Fig. 4(b). The power conversion efficiency drops quickly with the junction depth. For the passivated NW, the efficiency is less sensitive to the junction depth, and the optimal depth is around 1.8 μm.

Fig. 7(a) also shows the J–V curves for the Shockley–Queisser limit [39], either for perfect absorption (gray, dashed line) or simulated absorption (black, solid line). The short-circuit current of the passivated NW design is close to the Shockley–Queisser limit with simulated absorption, indicating efficient carrier collection. However, the open-circuit voltage is substantially lower than the Shockley–Queisser limit. This is mainly due to the low effective doping ($\sim 10^{16}$ cm$^{-3}$) in the intrinsic segment, which reduces the voltage drop across the p-n junction. However, the mobility increases with decreasing doping. As a result, the use of an intrinsic region, rather than a p-type doped region, also increases the minority carrier diffusion length and, thus, improves the minority carrier collection. The design represents a tradeoff between these two effects. We note that a high shell doping concentration is essential for achieving high efficiency. For a reduced shell doping concentration of $10^{17}$ cm$^{-3}$, the efficiency drops to 18.56% (compared with 21.26% at a shell doping of $10^{18}$ cm$^{-3}$). There is also a large discrepancy between the short-circuit current of the passivated NW design and the Shockley–Queisser limit assuming perfect absorption.
of photons above the bandgap of GaAs. This is mainly due to
the incomplete absorption of the photons [2].

Fig. 8 shows the short-circuit current, open-circuit voltage,
and efficiency as functions of the surface state density. We vary
the surface state density from $1.5 \times 10^9$ to $1.5 \times 10^{15}$ cm$^{-2}$,
corresponding to surface recombination velocities from 3 to
$3 \times 10^7$ cm/s. All three characteristics vary weakly as the sur-
f ace state density changes by six orders of magnitude.

VI. DISCUSSION

So far, we have assumed that the Shockley–Read–Hall re-
combination life time within the bulk is 1 ns, which is a rea-
sable estimate [32]. State-of-the-art growth techniques, such
as MOCVD [40], can produce GaAs with high material quality,
and the longest life time achieved in bulk structures is much
greater than 1 ns [41]. The bulk diffusion lengths of the mi-
nority electrons and holes used in the calculations above are
4.6 μm and 935 nm, respectively, and are comparable with the
nanowire height. However, for the bare nanowire, surface re-
combination effectively reduces the diffusion length below the
bulk value, preventing carriers from being collected at the con-
tacts. The key function of the AlGaAs passivation layer is to
prevent surface recombination, increasing collected current.

For shorter values of the bulk diffusion lengths, the efficiency
of the solar cell will decrease. To illustrate this, Fig. 9 shows
the power conversion efficiency as a function of junction depth for different bulk SRH recombination lifetimes. Fig. 9(a) shows the efficiency for the passivated nanowire structure. The blue curves are the same as the curves in Fig. 7(b). The red and black curves show the efficiency when the SRH lifetime is reduced to 0.1 and 0.01 ns, respectively. The corresponding minority electron diffusion lengths are 1.45 μm and 460 nm, respectively. The highest achievable efficiency drops with decrease in bulk diffusion length, and the optimal junction depth moves toward the top contact. When the diffusion length is shorter than the nanowire, placing the junction near the position where the most carriers are generated results in the largest current. Conversely, for larger values of the bulk diffusion length, the efficiency of the solar cell increases, and the optimal junction position moves toward the bottom of the wire, as shown by the green curve in Fig. 9(a). For the bare nanowire [shown in Fig. 9(b)], the efficiencies are lower than for the passivated nanowire, and this holds true for any value of the SRH lifetime. We conclude that surface passivation is a robust strategy for increasing efficiency across a range of material qualities.

One possible concern with a bare high-Al content AlGaAs layer is natural oxidation in the atmosphere. If this is a problem, one possible strategy is to reduce the Al content near the outer surface. Adding a thin GaAs outer layer is also an option [32]. The final device may also employ a polymer infill between the nanowires [4], which may inhibit nanowire oxidation.

VII. CONCLUSION

In this paper, we have designed a passivation scheme for axial junction nanowire-array solar cells. We used coupled optical and electrical transport simulations to validate our approach. We found that the absorption properties of the GaAs nanowire array with an AlGaAs passivation layer do not deviate much from the optimal bare GaAs nanowire design, due to the high bandgap energy of AlGaAs. Our design exhibits a 21.26% power conversion efficiency for the nanowire array with nonideal surface conditions, which is 2.7 times higher than the optimal bare nanowire design with the same surface conditions. The efficiency enhancement comes from the better protection of the generated minority carriers as well as the longer minority carrier diffusion length achieved by the modulation doping. The design also has great tolerance to the active layer doping concentration, surface conditions, and junction depth.

In this study, we designed a passivation layer specifically on a single-junction GaAs nanowire solar cell. The same concept can be applied to a nanowire multijunction tandem solar cell, with reoptimization for desirable band alignment by adjusting the shell’s composition and doping. Furthermore, since this design can greatly enhance effective minority carrier lifetime and conductivity, it can also be used in other nanowire applications such as photodetectors, light-emitting diodes, field effect transistors, and tunneling diodes.

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REFERENCES


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