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Absorption and transmission of light in III–V nanowire arrays for tandem solar cell applications

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Abstract

III–V semiconductor nanowires are a platform for next-generation photovoltaics. An interesting research direction is to embed a nanowire array in a transparent polymer, either to act as a standalone flexible solar cell, or to be stacked on top of a conventional Si bottom cell to create a tandem structure. To optimize the tandem cell performance, high energy photons should be absorbed in the nanowires whereas low energy photons should be transmitted to and absorbed in the Si cell. Here, through optical measurements on 1.95 eV bandgap GaInP nanowire arrays embedded in a polymer membrane, we identify two mechanisms that could be detrimental for the performance of the tandem cell. First, the Au particles used in the nanowire synthesis can absorb >50% of the low-energy photons, leading to a <40% transmittance, even though the Au particles cover <15% of the surface area. The removal of the Au particles can recover the transmission of low energy photons to >80%. Second, after the removal of the Au particles, a 40% reflectance peak shows up due to resonant back-scattering of light from in-plane waveguide modes. To avoid the excitation of these optical modes in the nanowire array, we propose to limit the pitch of the nanowire array.

Supplementary material for this article is available online

Keywords: III–V nanowires, absorption, transmission, photovoltaics

(Some figures may appear in colour only in the online journal)
polymer membrane has been demonstrated. However, the simultaneous absorption of high energy photons and transmission of low energy photons has not been studied. Here, we measured the absorption, reflection, and transmission of light in an array of GaInP nanowires embedded in a transparent polymer. The nanowires have a bandgap of \( \approx 1.95 \text{ eV} \), which is slightly larger than the 1.7 eV bandgap that is optimum for a top cell on top of a Si cell of 1.1 eV in bandgap [9]. However, for the purpose of this study, this \( \approx 1.95 \text{ eV} \) bandgap allows us to investigate the transparency properties in a larger wavelength range.

From the optical measurements, we identify two mechanisms that could be detrimental for the performance of a tandem cell based on such nanowires. First, the Au particles used in the nanowire epitaxy can absorb >50% of the low-energy photons, leading to a low <40% transmittance, even though the Au particles cover only 15% of the surface area. The removal of the Au particles can recover the transmittance of low-energy, below-bandgap photons to >80%. Second, after the Au particle removal, we observe a 40% reflectance peak due to back-scattering of light from in-plane waveguide modes. To avoid the excitation of these optical modes in the nanowire array, we propose to limit the array pitch, that is, the center-to-center distance between neighboring nanowires.

2. Methods

2.1. Nanowire growth

GaInP nanowires were grown from an Au (catalyst) particle array in a low pressure (100 mbar) metal-organic vapor phase epitaxy system (Aixtron 200/4) with a total flow of 131 m\(^{-1}\) and \( \text{H}_2 \) as the carrier gas. The Au particle array was defined on a 2\(^{nd} \) InP (111)B wafer by nanoimprint lithography, reactive ion etching, metal evaporation, and lift-off, resulting in a hexagonal pattern of Au particles with a pitch of 500 nm [23]. The imprinted InP wafer was cleaved into smaller samples used for growth.

The growth procedure of the GaInP nanowires can be described as follows: in order to improve pattern preservation, a pre-anneal nucleation step [23] was performed at 280 °C for 1 min with molar fraction of trimethylindium (TMIn) of \( \chi_{\text{TMIn}} = 8.9 \times 10^{-5} \) and phosphine (PH\(_3\)) of \( \chi_{\text{PH}_3} = 6.9 \times 10^{-3} \). Then the sample was heated to an annealing temperature of 550 °C where the sample was annealed for 10 min under \( \chi_{\text{PH}_3} = 3.5 \times 10^{-2} \) to desorb surface oxides. After annealing, the chamber was cooled to 460 °C. The growth was initiated with an InP nucleation step, by introducing TMIn at molar fraction of \( \chi_{\text{TMIn}} = 8.9 \times 10^{-5} \) and \( \text{PH}_3 \) at molar fraction of \( \chi_{\text{PH}_3} = 6.9 \times 10^{-3} \) to preserve pattern fidelity upon nanowire growth [23]. After 15 s, HCl was introduced at a molar fraction of \( \chi_{\text{HCl}} = 4.6 \times 10^{-5} \) to eliminate radial growth [24, 25]. After a total of 60 s of InP growth, GaInP growth was initiated by introducing trimethylgallium (TMGa) at a molar fraction of \( \chi_{\text{TMGa}} = 6.9 \times 10^{-4} \) and by switching the other precursor molar fractions to \( \chi_{\text{TMIn}} = 2.7 \times 10^{-3} \), \( \chi_{\text{PH}_3} = 5.4 \times 10^{-3} \), and \( \chi_{\text{HCl}} = 5.4 \times 10^{-5} \). The growth was then continued for 19 min while linearly ramping up the TMIn molar fraction to \( \chi_{\text{TMIn}} = 3.3 \times 10^{-3} \) in order to keep the composition constant throughout the GaInP segment (since the TMIn gas phase diffusion length is shorter than that of TMGa, the nanowires would become Ga rich towards the top with constant flows) [26].

After the growth of the GaInP segment, the TMIn precursor was switched off and a GaP segment was grown for 60 s at the top of the nanowire in order to reduce the growth of an InP segment during cool down. Note that a GaP segment is, due to its larger and indirect bandgap, preferential for our transparency studies compared to an InP segment (an InP segment can cause parasitic absorption in the transparency region of the GaInP). Finally, the flow of TMGa and HCl is switched off and the chamber is cooled to 300 °C under a \( \text{PH}_3/\text{H}_2 \) gas mixture. Note that after nanowire growth, the Au particles are alloyed with In. However, we will keep the term Au particle throughout the remaining text.

For this study, two samples were grown in the same growth run, positioned close to each other on a rotating susceptor, and hence experiencing nearly identical growth conditions. The Au particles were removed from one of the samples \textit{ex situ} by wet chemical etching in a KI:1\( \text{H}_2\text{O} \) solution after growth. The length and diameter of the as-grown nanowires were measured by SEM to be approximately 2300 nm and 186 nm, respectively (see figure 1(a)).

For the optical measurements, the samples were peeled off by embedding the nanowires into a flexible polymer (First Contact\textsuperscript{TM}), which shows negligible absorption of light at visible and near-infrared wavelengths (see supplementary information figure S1, available online at stacks.iop.org/NANO/28/205203/mmedia). For the peeling process, samples were bonded onto a 2 inch Si wafer by carbon tape. The colorless First Contact\textsuperscript{TM} polymer solution was applied on the samples with a pipette. Then the membrane was left in air for 24 h to dry out. Afterwards, the membrane was peeled by a tweezer which resulted in the nanowires being broken close to the nanowire–substrate interface (see figure 1(b) for a SEM image of the substrate after this peel-off process).

Room temperature photoluminescence measurements showed bandgap luminescence from the GaInP segment at \( \lambda \approx 640 \text{ nm} \), corresponding to a photon energy of approximately 1.95 eV (see supplementary information figure S2).

2.2. Absorption, reflection, and transmission measurements

We study the wavelength resolved absorptance \( A(\lambda) \), reflectance \( R(\lambda) \), and transmittance \( T(\lambda) \) of the samples. The absorptance shows the fraction of incident intensity that is absorbed by the sample. Similarly, the reflectance and the transmittance show the fraction of incident intensity that is reflected and transmitted, respectively.

Broadband \( R \) and \( T \) measurements were performed with an Avantes AvaSphere-30 integrating sphere. For details of the measurements, see [22]. The sample was placed just outside of the sphere to cover the \( \approx 5 \text{ mm} \) large measurement opening. Here, we used the light source and detector from a
Filmetrics F40 setup. The measurements were performed in the wavelength range of \(350 < \lambda < 1100\) nm with a spot size of approximately 2 mm in diameter.

From these \(R\) and \(T\) measurements, we can approximate the absorptance \(A\) through \(1 - R - T\) \([22]\). However, part of the scattered light is not detected with \(R\) or \(T\) measurements, leading to an overestimation of the absorption if \(A < 1 - R - T\) is used (see supplementary information figure S1). We assign this underestimation of \(R\) and \(T\) to some light being scattered beyond the 5 mm opening of the integrating sphere such that it is detected in neither \(R\) nor \(T\) measurements. To minimize such overestimation of \(A\), we performed dedicated absorption measurements with the sample placed inside a 2" Thorlabs IS-200 integrating sphere.

With the sample placed inside the sphere, all scattered light is expected to contribute to the measurement. To be able to insert the sample in the middle of the integrating sphere, we glued a paper clip onto the edge of each sample. We measured reference counts \(C_{\text{ref,abs}}(\lambda)\) when the sample was placed in the middle of the sphere with the incident light passing by the sample onto the inner wall of the sphere (see supplementary information figure S3 for schematics of the absorption measurements). Next, we measured \(C_{\text{sample,abs}}(\lambda)\) with light incident on the sample at approximately 10° angle from normal incidence. The absorptance was extracted as \(A(\lambda) = 1 - [C_{\text{sample,abs}}(\lambda) - C_{\text{dark,abs}}(\lambda)] / [C_{\text{ref,abs}}(\lambda) - C_{\text{dark,abs}}(\lambda)]\) with \(C_{\text{dark,abs}}(\lambda)\) being the dark counts when light was not incident into the sphere.

Note that in these measurements, we assume a homogeneous intensity distribution on the side walls of the integrating sphere. Such a distribution is enabled by multiple, diffuse scattering from the side walls of the integrating sphere. However, when we insert a sample inside the integrating sphere for the absorption measurements, we affect the propagation of that diffusively scattered light. By performing control measurements on Si substrate samples of varying size, we found that the measured absorptance was independent of sample size up to a sample size of \(15 \times 15\) mm\(^2\) (see supplementary Information figure S4). The two GaInP nanowire array samples in this study were each approximately \(7 \times 7\) mm\(^2\) in size. We present results for light incident toward the nanowire stubs exposed to air (see figure 2). The main spectral dependencies and conclusions were independent of the illumination side.

3. Results

As described above, we measured the absorptance, reflectance, and transmittance of the nanowire arrays for \(350 < \lambda < 1100\) nm. The wavelength of 1100 nm matches well to the 1.1 eV bandgap of Si. Hence, we investigate a wavelength range that is relevant for a nanowires-on-Si tandem cell.

Absorption in nanowires with Au particle is shown in figure 3(a) by the blue line. For \(\lambda < 650\) nm, we observe strong absorption, which we assign to the GaInP main part of the nanowires, which has a bandgap wavelength of \(\approx 640\) nm (see supplementary information figure S2). Here, we find peak values of \(A > 80\%\). In the wavelength range of \(700 < \lambda < 900\) nm, we find a much lower absorptance with \(A < 20\%\). We assign this absorption to the \(\approx 100\) nm long InP stub (see figure 2). For \(\lambda > 900\) nm, we find that the measured absorptance is very close to zero, as expected since the bandgap wavelength of bulk InP is \(\approx 925\) nm.

Absorption in nanowires with Au particle is shown in figure 3(a) by the red line. Again, for \(\lambda < 650\) nm, we find a strong absorption in the range of \(A \approx 80\%\). However, at longer wavelengths we observe high absorptance values in the range of 40%--60%. Thus, the Au particles enable considerable absorption, even at \(\lambda > 925\) nm where the nanowires are not expected to absorb. As a control experiment, we have performed measurements on pure InP nanowires. Also
there, a similar difference in absorption with and without the Au particles was observed at $\lambda > 925$ nm where the InP nanowires are not expected to absorb noticeably (supplementary information figure S5).

To understand this large difference in absorption properties caused by the Au particle, we turn to study the transmission and reflection of the samples (figures 3(b) and (c)). For both samples, we find low transmittance for $\lambda < 650$ nm, as expected from the strong absorption ($A \approx 80\%$) of the samples. The transmittance for the sample without the Au particles increases to $T > 80\%$ for $\lambda > 950$ nm. In contrast, the transmittance in the sample with Au particles stays at $T < 45\%$ even at $\lambda = 1100$ nm. Regarding the reflection, we find $R \approx 10\%$ in general for both samples, except for the sample without Au particles when $650 < \lambda < 900$ nm. In this wavelength range, we find a higher reflectance that peaks at $R \approx 40\%$ for $\lambda \approx 750$ nm. Note that this $R \approx 40\%$ is actually higher than the $R \approx 30\%$ of a planar semiconductor/air interface, assuming normal incidence and a refractive index of 3.5 for the semiconductor. As an additional observation, we see that $1 - R - T > A$ for both samples (see supplementary information figure S1 for a clearer comparison).

The above behavior of $R$, $T$, and $A$ can be explained by a coupling of incident light into in-plane waveguide modes that propagate in the plane of the nanowire array (marked by (4) in figure 4). The nanowire array has a higher effective refractive index than the air above and the polymer below, which is the condition required for such in-plane waveguiding [27]. Note that the HE$_{11w}$ waveguide modes, which lead to optimized absorption in nanowire arrays [12], propagate along the axis of the nanowires, that is, perpendicular to these in-plane waveguide modes.

At long wavelengths of $\lambda > 925$ nm for the sample without the Au particles, where the nanowires do not absorb light noticeably as seen from $A$ measurements, we believe that the in-plane waveguiding can propagate some of the light for a considerable distance along the array before scattering out. The light that is propagated beyond the 5 mm large entrance opening of the integrating sphere before scattering out of the array will not contribute to $R$ or $T$ measurements, leading to $1 - R - T > 0$ even though $A \approx 0$ (see supplementary information figure S1). That is, the in-plane waveguide modes can function to trap light into the nanowire array. At shorter wavelengths, such in-plane waveguiding can in principle enhance the absorption because the light interacts for a longer time with the absorbing nanowires.

We assign the peak in the reflectance at $\lambda \approx 750$ nm for the sample without Au particles (blue line in figure 3(c)) to back-scattering from such in-plane waveguide modes. In more detail, we depict that at this wavelength, a large fraction of the incident light intensity is coupled into the in-plane waveguide modes. That is, the in-plane waveguide modes are excited resonantly. However, a large fraction of that light can scatter out of these waveguide modes either (1) back to the top side giving rise to enhanced reflection or (2) into the membrane, before getting absorbed by the nanowires. In support of this reasoning, electromagnetic modeling of the interaction of light with a polymer-embedded nanowire array of 500 nm pitch indicates a resonant reflection peak at $\lambda \approx 750$ nm (see supplementary information figure S6).
Next, for the sample with Au particles still present, we consider the strong \( \approx 50\% \) broadband absorption at \( \lambda > 650 \text{ nm} \) and the lack of the peak in the reflection at \( \lambda \approx 750 \text{ nm} \)—a peak that was seen without the Au particles. We believe that both of these effects are associated with (i) the coupling of incident light to the in-plane waveguide modes and (ii) the consecutive absorption of this wave-guided light in the Au particles. We expect that the in-plane waveguide modes can travel for a considerable distance along the array, leading to a strong absorption in the Au particles, explaining the \( \approx 50\% \) absorption. However, at the same time, the strong absorption in the Au particles is expected to limit the possibility to resonantly excite the waveguide modes. Thus, we believe that the Au particles lead to a weaker resonant excitation of the waveguide modes at \( \lambda \approx 750 \text{ nm} \) and consecutively to a weaker back-scattering, which explains why we do not observe a peak in \( R \) at \( \lambda \approx 750 \text{ nm} \) when the Au particles are present.

In principle, additional light trapping could occur due to scattering of transmitted light inside the membrane to angles beyond the critical angle of \( \sin(n_{\text{membrane}}/\sin(n_{\text{air}}) = 42^\circ \) for the refractive indexes \( n_{\text{membrane}} \approx 1.5 \) and \( n_{\text{air}} \approx 1 \). Such light is expected to experience total internal reflection at the bottom interface between the membrane and the air beneath. After the total internal reflection, the light could interact with the nanowire array again.

4. Discussion and outlook

When we include a metal like Au into our nanowire system, we expect an increase in the reflection [15, 28]. However, as presented above, the observed main optical effect of the Au particles is a 50\% broadband absorption, even though the Au particles cover only \(< 15\% \) of the area in the plane of the nanowire array. Thus, the Au particles can lead to a more complicated optical response than just mere reflection losses.

We showed that these absorption losses due to the Au particles could be eliminated by simply removing the Au particles before embedding the nanowires in the membrane. However, when the Au particles were removed, a reflection loss, peaking at 40\%, showed up. We assigned this reflection peak to (i) resonant coupling of incident light into in-plane waveguide modes (see figure 4) and (ii) consecutive, partial scattering of that light back into the incidence side. We note that in Si nanowire arrays, such in-plane modes can be used for enhancing the absorption in the wavelength range of indirect optical transitions where Si absorbs weakly due to the indirect bandgap [29]. However, in a tandem solar cell architecture, it is important to avoid the excitation of such modes in the wavelength region where the nanowires are non-absorbing, to allow transmission of long wavelength light into the subcell(s) below.

We expect that the in-plane waveguide modes shift up in energy when the array pitch is decreased [27]. Indeed, by decreasing the pitch of the nanowire array, we find from electromagnetic modeling that the region of resonant reflection moves toward shorter wavelengths, that is, toward higher energy (supplementary information figure S6).

Once the material, and hence the bandgap, for the nanowires is chosen, we know at which wavelength the transparency region of the nanowire-array subcell starts. We propose that the array pitch should be chosen small enough so that the in-plane waveguide modes are not resonantly excited in that long-wavelength transparency region. Note that the strong absorption in the nanowires in the short wavelength region should prohibit the resonant excitation of the in-plane waveguide modes. Therefore, we expect that the in-plane waveguide modes can be shifted to this short wavelength region without leading to noticeable reflection losses there. In support for this reasoning, no noticeable effects from resonant reflection have been identified in the absorption modeling of direct bandgap III–V nanowire arrays [10–16].

To summarize, we see great prospect in III–V nanowire arrays for tandem solar cell applications. In a GaInP nanowire array embedded in a polymer membrane we have demonstrated a simultaneous \( > 80\% \) absorption of above bandgap photons and a \( > 80\% \) transmission of below bandgap photons. We expect that a detailed geometry optimization [12] of the nanowire array geometry could enhance this absorption and transmission further. In such optimization, we should also include the effect of transparent conductive oxide layers, which are used for electrically contacting the nanowire sub-cell. Furthermore, if the nanowire subcell is planned to be stacked immediately on top of a high refractive index Si cell without additional encapsulation layers, the Si cell should be included in the analysis of the optical response of the nanowire array.

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