Quantifying limits and losses in nanoscale photovoltaics

Mann, S.A.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Nanoscale materials are promising for optoelectronic devices because their physical dimensions are on the order of the wavelength of light. This leads to a variety of complex optical phenomena, that for instance enhance absorption and emission. However, quantifying the performance of these nanoscale devices frequently requires measuring absolute absorption at the nanoscale and, remarkably, there is no general method capable of doing so directly. Here we present such a method based on an integrating sphere, but modified to achieve diffraction-limited spatial resolution. We explore the limits of this technique by using it to measure spatial and spectral absorptance profiles on a wide variety of nanoscale systems including different combinations of weakly and strongly absorbing and scattering nanomaterials (Si and GaAs nanowires, Au nanoparticles). This measurement technique provides quantitative information about local optical properties that are crucial for improving any optoelectronic device with nanoscale dimensions or nanoscale surface texturing.
5 Integrating sphere microscopy

5.1 Introduction

A number of techniques to measure quantitative absorptance on single nanostructures exist [90–92], such as photothermal spectroscopy [88, 106, 107, 191], (spatial modulation) extinction spectroscopy [94, 99, 102], and scattered field interferometry [89]. Although some of these techniques are extremely sensitive and can even measure single molecules [87], they also rely on at least one of the following assumptions: all absorbed power is converted into heat, the nanoparticle doesn’t scatter light, or it interacts with light as an ideal dipole. Hence, to date there is no generally applicable method available for quantitative absorption measurements of nanostructures, even though for instance nanostructured semiconductor and plasmonic hot-electron optoelectronic devices [192, 193] require such a technique to quantify their performance.

Here we show that by combining an integrating sphere with an ultra-long working distance microscope objective, we can achieve submicron spatial resolution inside the integrating sphere. As a result, quantitative local absorptance measurements can be obtained, even on single nanostructures. In this chapter we detail the working mechanism and explore the limits of integrating sphere microscopy using weakly absorbing but strongly scattering structures (a silicon nanowire and a large gold nanoparticle), a weakly absorbing and weakly scattering structure (a small gold nanoparticle), and a strongly absorbing and strongly scattering structure (a GaAs nanowire). Additionally, we demonstrate the spatial resolution with absorption maps on a highly tapered nanowire where resonances can be seen moving along the length as a function of wavelength.

5.2 Integrating sphere microscopy

Single nanoparticle spectroscopy relies on illumination with a focused beam to enhance the interaction with the nanoparticle. When illuminating a nanoparticle, part of the power will be absorbed or scattered by the nanoparticle ($P_{\text{abs}}$ and $P_{\text{sca}}$, see Section 1.3 on page 19). Additionally, even for a focused beam the majority of the incident power will typically not interact with the nanoparticle and be either transmitted or reflected ($P_T$ and $P_R$). Just as with the standard integrating sphere method [194, 195], integrating sphere microscopy relies on determining the scattered, transmitted, and reflected light, such that the absorbed power can be inferred: $P_{\text{abs}} = P_{\text{in}} - P_R - P_T - P_{\text{sca}}$. To do so with submicron resolution, we combined an integrating sphere with a ultra-long working distance microscope objective, which focuses the light on the sample inside the integrating sphere (see Fig. 5.1a). The sample is mounted on a 3D piezoelectric stage, which allows scanning of the sample to obtain quantitative local information of the absorptance. The ability to scan the focus with respect to the sample is crucial: without scanning, integrating sphere microscopy can only be used in a wide field configuration, which does not allow for quantitative spatial information [196]. Finally, broadband char-
Figure 5.1: Schematic of the integrating sphere set-up. a. Schematic depiction of the combination of microscope objective and integrating sphere. The objective focuses light on the sample holder inside the integrating sphere, and the photodetector is behind a baffle on the backside of the integrating sphere. b. Schematic diagram for the experimental set-up, including reflection photodetector (PD) and half-wave plate to control the polarization. BS stands for beam splitter and BM for beam monitor, which we use to account for fluctuations in laser power.

Characterization is possible, since we use a supercontinuum laser as a light source (400-2000 nm), and the integrating sphere inner surface remains Lambertian from 250-2500 nm.

A detector behind a baffle on the backside of the integrating sphere measures transmitted and most of the scattered power, while the reflected and backscattered power is collected back through the objective and measured by a second photodetector (see Fig. 5.1b). For the absorptance we then obtain:

\[ A = 1 - \frac{R}{R_{\text{ref}}} - \frac{I_{S}}{I_{S_{\text{ref}}} - C}, \]  

(5.1)

where \( R \) and \( R_{\text{ref}} \) are the reflection signal and reference measurement, and \( I_{S} \) and \( I_{S_{\text{ref}}} \) are the integrating sphere signal and reference measurement. Calibration of the technique is thus extremely simple: it only requires two reference measurements, usually a mirror for \( R_{\text{ref}} \) and a small hole in the substrate for \( I_{S_{\text{ref}}} \) (meaning that the beam misses the sample, but the sample is still in the integrating sphere). \( C \) in Eq. 5.1 is an offset that arises from the reflection of the second interface of the glass sample holder, which is collected by the objective but so far out of the focal plane that it is not imaged on the photodetector. For glass \( C \approx 0.04 \) (the reflection of a single air-glass interface), but it depends slightly on how much power is transmitted and scattered forward, and assuming that it is constant therefore introduces a small source of error. The accuracy of the technique additionally depends on the detection efficiency of all non-absorbed light: e.g., if some light is scattered but not detected by either photodetector, it will appear as absorption. Based on measurements on non-absorbing but strongly scattering silica beads we
estimate that $95 \pm 1.2\%$ of the total scattered power is collected (see Supplementary Information, Section 5.6.3).

5.3 Nanowire absorption measurements

5.3.1 Silicon nanowires

We will now demonstrate this technique by showing local variation in the absorptance of a tapered silicon nanowire. Semiconductor nanowires are important building blocks for optoelectronics applications [197], including nanowire solar cells [51, 53], light-emitting diodes [123, 198, 199], lasers [200], and quantum information technology [201]. Fig. 5.2a shows an SEM image of a 10 $\mu$m long silicon nanowire on a glass substrate. The nanowire is slightly tapered, with a diameter that varies from 160 nm at the top of the image to 95 nm at the bottom. Fig. 5.2b displays the
5.3 Nanowire absorption measurements

Figure 5.3: Absorption spectra of a silicon nanowire. a, SEM image of the silicon nanowire indicating the positions at which spectra were measured. The scale bar is 1 µm. b, The measured absorption cross section of the silicon nanowire at position 1 with the electric field polarized along the nanowire axis, compared to simulations of a hexagonal nanowire on glass with an apothem of 68 nm (blue line, see Supplementary Information Section 5.6.5 for details). The inset shows the simulated absorption cross section (blue) compared to the scattering cross section (red), indicating that the wire scatters much more strongly than it absorbs. c, Same as in panel b but with the electric field polarized perpendicular to the axis. d-e, Same as panels b and c, but measured at position 2 and with 48 nm apothem hexagonal nanowire simulation. In b-e the error bars are due to variance in the absorptance and uncertainty in the conversion to cross section.

absorptance $A$ (absorbed fraction of the incident power, $A = P_{\text{abs}}/P_{\text{in}}$) at a wavelength of 450 nm, measured while scanning over the area shown in the SEM image using the 3D piezoelectric stage. In the center of the wire a peak in absorptance is visible, which corresponds to resonantly enhanced absorption via a Mie (geometrical) resonance. Mie resonances shift to longer wavelengths as the radius of the wire is increased, as they occur for fixed values of the product $nk_0r$, where $n$, $k_0$, and $r$ are the refractive index, free space wavenumber and radius [202]. The absorption maps in Fig. 5.2c-f show the peak moving from smaller to larger diameter along the tapered nanowire as the illumination wavelength increases, providing a direct visualization of these diameter-dependent resonance phenomena.

Fig. 5.2g plots absorption intensity line cuts along the tapered nanowire in Fig. 5.2c-f, together with calculated dispersion relations to identify the relevant Mie resonances (see Chapter 7, Section 7.6.2). These resonances can be specified with the notation $TM_{ml}$, where TM indicates the magnetic field is transverse to the long axis of the nanowire, $m$ is the azimuthal mode number, corresponding to the
number of field maxima around the nanowire circumference, and $l$ indicates the number of radial field maxima. From these calculations shown in Fig. 5.2g it is clear that we observe the TM$^{21}$ and TM$^{12}$ resonances. These resonances are nearly degenerate and hard to disentangle spatially.

In addition to measuring nanoscale absorption maps at a fixed wavelength, we can also fix the laser position and measure local absorption spectra. Fig. 5.3a shows an SEM image of the same nanowire (but rotated) and indicates two positions where spectra were measured. Figs. 3b-e show the wavelength-dependent absorption cross sections of the nanowire at the two different positions, with the laser polarized either along or orthogonal to the nanowire axis. A geometric scaling factor is used to convert from absorptance to cross section: $\sigma_{abs} = A\sqrt{\pi w_0^2/2}$, where $A$ is absorptance and $w_0$ is the beam radius. This factor can be derived by assuming that the nanowire is infinitely thin, and integrating the Gaussian spot intensity over the nanowire length. While the nanowire is not infinitely thin, agreement with full-wave simulations is good (see Supplementary Information, Section 5.6.1). However, because the scattered power significantly exceeds the absorption by up to a factor of 75, disagreement between the measurement and full-wave simulations is likely due to the small fraction of scattered light that is not detected.

### 5.3.2 GaAs nanowires

Due to the indirect band gap of silicon, these nanowires scatter very strongly, and they therefore provide a particularly challenging test case. Agreement with theory is even better for more strongly absorbing materials such as GaAs, as we will show now. Fig. 5.4a shows an SEM image of a GaAs nanowire with a radius ranging from 110 nm at the top of the image to 84 nm at the bottom. Figures 5.4b-f show absorption maps for different wavelengths, just as for the silicon nanowire. However, since this nanowire has a lower tapering angle the resonances do not appear localized along the nanowire length. Additionally, the nanowire has a smaller diameter, which means that a lower order resonance is excited (the TM$^{11}$ resonance), which has a broader linewidth and, interestingly, therefore also a larger spatial extent in a tapered nanowire than a resonance with a narrower linewidth would have. Fig. 5.4g and 5.4h show the cross section versus wavelength, compared to full-wave simulations of the nanowire absorption and extinction cross section for parallel and perpendicular incident polarizations, measured at the top of the wire. Both spectra show a resonance at 480 nm, which are the TM$^{11}$ and TE$^{01}$ resonances in the parallel and perpendicular polarization respectively. Since GaAs has a direct band gap, the scattering cross section is reduced and the absorption cross section is increased, indeed improving the agreement with numerical predictions.
5.4 Au nanoparticles

Due to the linear extent of the nanowire, the intersection with the focused spot is significant and measurements above the noise floor are therefore easily achieved. To probe the detection limits of our set-up, we also investigate small spherical gold nanospheres with a plasmon resonance near 500 nm. While the absorptance of...
the nanowires reaches >10% easily, the absorptance of a 60 nm gold sphere will lie below 1% due to the small absorption cross section. Since the nanoparticle is localized in three dimensions, we now obtain for the absorptance (assuming that the nanoparticle can be treated as a point): \( A(x, y) = \sigma_{\text{abs}} I(x, y) \), where \( I(x, y) \) is the intensity distribution in the Gaussian spot. If the nanoparticle lies exactly in the focus, we find \( \sigma_{\text{abs}} = A \times \pi w_0^2/2 \), where we used \( I(x = 0, y = 0) = 2P_{\text{in}}/\pi w_0^2 \) and \( A = P_{\text{abs}}/P_{\text{in}} \). This absorption cross section is shown in Fig. 5.5a for a 60 nm diameter gold sphere and in Fig. 5.5b for a 200 nm diameter gold sphere.

Even though the absorptance peaks at 0.5% for the 60 nm diameter nanosphere, the noise floor is low enough for accurate determination of the absorption cross section. In fact, the error margin shown in Fig. 5.5 arises largely due to the determination of the Gaussian beam radius \( w_0 \). For the absorptance measurements the signal-to-noise ratio (determined as the peak absorptance relative to the standard deviation of the baseline) is 530 for the 200 nm diameter sphere and 30 for the 60 nm sphere. The noise level relative to the total measured power is \( 5 \times 10^{-5} \), which is comparable to the relative intensity noise (RIN) of supercontinuum lasers \( (1.5 \times 10^{-5}) \) as reported in Ref. [95]. These measurements were done using lock-in amplifiers with a measurement bandwidth of 780 mHz (100 ms time constant and 24 dB/oct roll-off). The noise floor can be reduced further by using low noise lasers, but at the cost of the broad bandwidth, since supercontinuum lasers are inherently noisy [203]. Furthermore, tighter foci, longer integration times, or balanced detection schemes can also help, but the noise floor is clearly already sufficiently low to measure the absorption of a single small gold particle.
5.5 Conclusion

To conclude, we have introduced a new technique to perform quantitative and spatially resolved absorption spectroscopy on single scattering nanoparticles. The technique uses an integrating sphere to measure directly the transmitted, reflected, and scattered power, allowing for determination of the absorbed power. Calibration of the absorption measurement is very straightforward and no assumptions on the nature of the scattering particle are required. We demonstrated integrating sphere microscopy by mapping the absorption cross section of tapered silicon and GaAs nanowires. These are essential characteristics for many optoelectronic devices, in particular for LEDs and solar cells, but can not be measured on the nanoscale with photothermal spectroscopy or any other known method. We therefore believe that this extension of the standard integrating sphere measurement to nanoscale systems can be of great utility in nanoscale optoelectronics, single nanoparticle spectroscopy, and other fields where quantitative and high spatial resolution measurements are desired.

5.6 Supplementary Information

5.6.1 Conversion from absorptance to cross section

The equation to convert from absorptance to cross section can be found by considering the Gaussian intensity distribution of the focused spot:

\[
I(x, z) = I_G \exp\left(-2\left(\frac{x^2 + z^2}{w_0^2}\right)\right) = \frac{2P_{\text{in}}}{\pi w_0^2} \exp\left(-2\left(\frac{x^2 + z^2}{w_0^2}\right)\right),
\]

where \(I_G\) is the Gaussian peak intensity and \(P_{\text{in}}\) is the total power carried by the beam. The beam waist \(w_0\) is defined as the radius at which the intensity is \(I_G/e^2\). When the wire is subject to inhomogeneous illumination, as with a Gaussian spot, the total absorbed power is found by integrating the intensity along the nanowire, where we assume that we can ignore the field gradient over the width of the nanowire (i.e. the wire is infinitely thin):

\[
P_{\text{abs}} = \int \sigma_{\text{abs}} I(x = 0, z) dz = \sigma_{\text{abs}} P_{\text{in}} \sqrt{\frac{2}{\pi w_0^2}},
\]

where for simplicity we assume that the wire is aligned along the \(z\)-axis, and that the cross section does not depend on position along the nanowire. Note that for tapered wires this is an approximation. From Eq. 5.3 we obtain:

\[
\sigma_{\text{abs}} = \frac{P_{\text{abs}}}{P_{\text{in}}} w_0 \sqrt{\frac{\pi}{2}} = A w_0 \sqrt{\frac{\pi}{2}}.
\]

This formula has been applied before to carbon nanotubes [94]. Although the assumption is made that the wire is infinitely thin, the agreement between
5 Integrating sphere microscopy

Figure 5.6: Numerical verification of the conversion from absorptance to cross section. Using finite-difference time-domain (FDTD, Lumerical [140]) we determined the absorption in a hexagonal GaAs nanowire with apothem of 46 nm on a glass substrate when positioned in the focus of a Gaussian beam (NA=0.25), as shown in blue and red dashed lines. We compare this to total-field scattered-field plane wave simulations to obtain the actual cross section $\sigma_{\text{abs}}$ (gray solid lines), which shows excellent agreement with the Gaussian beam simulations.

Gaussian beam and plane wave simulations using this formula is excellent even for nanowires with a diameter of 100 nm and a beam waist of 570-760 nm (see Fig. 5.6).

Knife edge measurements

To determine the spot size we performed standard knife edge measurements, as described in e.g. Ref. [204]. The measurements were performed on a gold film with sharp edges on glass. The reflectivity is recorded as a function of position, resulting in a curve with the typical error function shape (see blue circles in Fig. 5.7a). The derivative of the reflectance (shown in red circles) is fit with the Gaussian intensity along one axis:

$$f(x) = a \exp \left( -2 \left( \frac{x - x_0}{w_0} \right)^2 \right),$$

(5.5)

where $a$ is a fitting parameter for the height, $x_0$ for the position of the knife edge, and $w_0$ for the beam waist. The fit is also shown in Fig. 5.7a (red solid line), and is in good agreement with the measurement. This fitting procedure is performed for different wavelengths and for two directions (horizontal and vertical), the results of which are shown in Fig. 5.7b. The measurements indicate a slightly elliptical spot size, with the spot elongated in the vertical direction. The error bars in Fig. 5.7b indicate the 68% confidence interval.
5.6 Supplementary Information

Figure 5.7: Knife edge measurements to determine the beam waist. a. Recorded reflection while scanning over a sharp edge of a gold film on glass (blue) at 500 nm wavelength. The derivative (red dots) shows the beam profile together with the fit (red solid line). b. Retrieved spot sizes as a function of wavelength for two scanning directions (vertical in red and horizontal in blue). This indicates that the spot is slightly elliptical. The increase in spot size is linear with an NA of 0.25 averaged over both scan directions.

5.6.2 Error propagation

The error on the measured absorption cross sections in Figs. 5.3, 5.4, and 5.5 in the main text is due to noise in the measured absorptance values $\delta A$, as well due to uncertainty in the spot size conversion. Since the absorption measurements themselves can be too lengthy to repeat many times we estimate the uncertainty in the measurement from the standard deviation in 50 values of $R$ and $I S$ that were measured next to a nanoparticle. Then, we obtain for the uncertainty in the absorption measurement [205]:

$$
\delta A = \sqrt{(\delta IS)^2 + (\delta R)^2}.
$$

For the conversion to cross section we assume that the 68% confidence interval from the fit algorithm (see previous section) is representative of the uncertainty. This then gives for the total error:

$$
\delta \sigma_{\text{abs}} = \sigma_{\text{abs}} \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta w_0}{w_0}\right)^2}.
$$

5.6.3 Non-absorbing silica bead measurements

To examine the detection efficiency of scattered light in the integrating sphere microscopy setup, we have measured these detection losses on a SiO$_2$ nanosphere with a 460 nm diameter (see Fig. 5.8a), which strongly scatters but does not absorb. Figs. 5.8b and 5.8c show the reflection and integrating sphere maps, respectively,
Figure 5.8: Examination of accuracy based on a non-absorbing particle. a. SEM image of a silica nanosphere with a diameter of 460 nm. b,c. Reflection and integrating sphere signal of the same nanosphere at 600 nm wavelength. d. Maps in b and c combined to give the absorptance map, showing that only a small fraction of the scattered power is not detected. The scale bar in a-d is 1 µm. e. The extinction cross section of the nanosphere (blue dots) together with the Mie theory cross section (blue line). Red dots show the measured detection losses, indicating that 95.2 ± 1.2% of the scattered light is detected. Error is due to variance and uncertainty in the cross section conversion (see Section 5.6.2).

for the nanosphere. The 2% decrease in reflection is matched by an analogous increase in the integrating sphere signal, but as shown in Fig. 5.8d a small difference remains when reflection and integrating sphere signals are combined. The maximum of this detection loss is shown as an effective detection loss cross section for a range of wavelengths in Fig. 5.8e. This figure also shows the extinction cross section measured on the same nanosphere (blue points), which we determined by measuring transmission of the focused light using a second microscope objective facing the excitation objective (see Section 5.6.6). Following the same approach as for $\sigma_{\text{abs}}$ for the gold nanospheres, we find $\sigma_{\text{ext}} = (\Delta T/T) \times \pi w^2_0/2$. The extinction measurements agree very well with the theoretical extinction cross section from Mie theory for a 460 nm SiO$_2$ sphere in vacuum (blue line, equal to the scattering cross section since the nanoparticle does not absorb). Based on the ratio of detection loss to extinction we estimate that 95 ± 1.2% of the scattered power is collected. This is higher than what can be detected with other methods. For example, for microscope objectives with the highest possible numerical aperture, the acceptance half-angle is practically limited to about 75 degrees. As a result, in the standard extinction setup with two objectives facing each other, only 80% of the power scattered by a simple dipole in a homogeneous environment can be collected [206].

Although the collection efficiency is already quite high, we believe it can be further increased. In our current set-up, there appear to be two major loss mechanisms: 1) the outer few millimeters of the objective front lens do not contribute to
laser light focusing or collection, but are also not covered by the integrating sphere; and 2) light that is scattered within the critical angle of the glass substrate might be guided out of the integrating sphere through the sample port. We believe that both losses can be mitigated with an improved integrating sphere and sample holder design, such that collection efficiencies even higher than 95% may be achieved.

5.6.4 Sample preparation

The silicon nanowires are grown epitaxially on a silicon substrate by the vapor-liquid-solid growth mechanism using an atmospheric-pressure chemical vapor deposition system. 40 nm gold particles were used as catalysts. The growth was conducted at 800 °C for 5 minutes with silicon tetrachloride (SiCl₄) as the precursor. The carrier-gas flows during growth are Ar=200 Standard Cubic Centimeters per Minute (SCCM) and H₂=50 SCCM, while only 75 SCCM Ar gas flows directly through the silicon tetrachloride precursor bubbler (held at 0 °C in a temperature-controlled bath). Self-catalyzed GaAs nanowires were grown by solid-source III-V MBE directly on p-type Si(100) substrates by solid-source III-V Veeco molecular beam epitaxy (MBE) GEN-930. The nanowires were grown with a Ga beam equivalent pressure of 8.7×10⁻⁸ Torr, a V/III flux ratio of 50, a substrate temperature of 630 °C, and a growth duration of 1 hour. The substrate temperature was measured with a pyrometer. The gold nanoparticles (60 nm and 200 nm diameter) were acquired from BBI solutions.

5.6.5 Simulations

The nanowire cross section simulations were performed with Lumerical FDTD [140]. The nanowire had a hexagonal shape and was assumed to be infinitely long (the simulations were 2D). The refractive index of silicon and GaAs was based on tabulated data from Palik [207]. In both the calculations of the dispersion diagrams and simulations the parallel momentum was assumed to be zero, treating the wire as if illuminated under normal incidence. Considering the low NA (0.42) in the experiment this is an accurate assumption.

5.6.6 Experimental setup

The light source in the experiment was a supercontinuum laser (Fianium WL-SC-390-3), which was made monochromatic using an acousto-optical tunable filter (AOTF, Crystal Technologies). Power in the focused laser beam is on the order of several to tens of μW. The microscope objective is a 17 mm working distance Mitutoyo M Apo Plan NIR 50x with NA=0.42. The integrating sphere is a LabSphere GPS-020-SL, modified so that it can accommodate our objective lens. The photodetectors are Thorlabs amplified Si detectors (PDA100A), read out by Stanford Research Systems SR830 lock-in amplifiers. For the Au NP measurements the IS photodetector was replaced by a passive Newport 818-UV photodetector, which
5 Integrating sphere microscopy

has a lower noise level than the Thorlabs transimpedance amplifiers. The trans-
mmission of the AOTF was digitally modulated at 20 kHz with a 50 percent duty
ycle for the nanowire measurements, and at 700 Hz for the Au NP measurements.
The sample holder is mounted on a Piezojena Tritor400 3D piezoelectric stage for
high resolution scanning of the sample, while for rough alignment the piezoelectric
stage itself is mounted on a Newport mechanical stage. For the extinction mea-
surements on the silica beads in Fig. 5.8 we used a Nikon T Plan EPI SLWD 50X
0.4 NA objective for collection, which imaged the transmitted light on a PDA100A
amplified photodetector.