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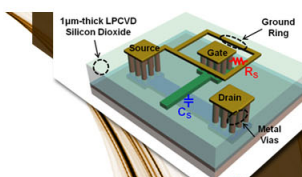
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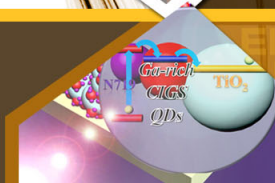
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Measurement of light diffusion in ZnO nanowire forests

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Optimum design of efficient nanowire solar cells requires better understanding of light diffusion in a nanowire array. Here we demonstrate that our recently developed ultrafast all-optical shutter can be used to directly measure the dwell time of light in a nanowire array. Our measurements on disordered ZnO nanowire arrays, “nanowire forests,” indicate that the photon mean free path and the dwell time of light can be well predicted from SEM images. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692741>]

Nanowire solar cells are promising devices for solar energy conversion.¹ They are inexpensive because of the small amount of material needed and are efficient because of strong light absorption and rapid carrier collection. In the past few years, photovoltaic devices have been reported based on arrays of dye-sensitized ZnO nanowires,^{2,3} nanoflowers,⁴ nanotrees,⁵ silicon nanowires,^{6,7} nanocones,⁸ microwires,⁹ CdS nanopillars,¹⁰ and multi-layered nanopillars¹¹ and nanorods.¹²

The enhanced optical absorption of these photovoltaic devices compared to planar solar cells can be attributed to three effects. First, the reflectivity is reduced.^{13–16} Second, nanowires capture and confine incoming light into guided modes, leading to concentration of the electromagnetic field inside the absorbing material.^{11,16–19} Third, light travels a long diffusive path through the nanowire array, as a result of multiple scattering between the wires. A photon not converted to an electron-hole pair in a first nanowire hit gets many additional chances.

This diffusion effect has been experimentally studied by static optical reflection and absorption measurements and current-voltage characterization of solar cells.^{7,14} For a good understanding of the light diffusion dynamics, however, time-resolved measurements also are needed. Powerful interferometric methods have been developed to measure the transport of light through strongly scattering media.^{20,21} Application of these methods is, however, quite difficult because of the advanced optical setup needed, the speckle by speckle measurement, and the complicated data analysis.

In this letter, we present a simple method to directly measure the diffusive dwell time of light in a disordered ZnO nanowire array, a “nanowire forest.” The measured dwell times of light turn out to be reasonably well accounted for by a simple ray-optics diffusion model. In this model, the photon mean free path (MFP) is estimated from scanning electron microscope (SEM) images of the nanowire forests. Consequently, SEM images can be used to predict the light diffusion in this type of samples and to optimize the solar cell performance.

For the measurements of the dwell time, we use our recently developed ultrafast all-optical shutter,²² with a ZnO

nanowire forest replacing the ZnO single crystal. Two 125-fs laser pulses, a strong 800-nm gating pulse and a weaker probe pulse with a wavelength between 385 and 415 nm, are sent through the ZnO nanowire forest with a variable delay. If the delay is such that the pulses are simultaneously present inside the sample, two-photon absorption of a probe photon and a gating photon occurs. Measurement of the probe transmission as a function of delay reveals the time photons spend inside the sample.

We have performed measurements on two disordered ZnO nanowire arrays (Fig. 1). Note that disorder in the position of nanowires has been shown to enhance the absorption of light.²³ The nanowire forests were epitaxially grown on sapphire substrates using the carbothermal reduction method with gold particles as catalysts.²⁴ In the furnace, first a porous ZnO seed film grows on the sapphire crystal. On top of that film the nanowires emerge, with their *c*-axes parallel to

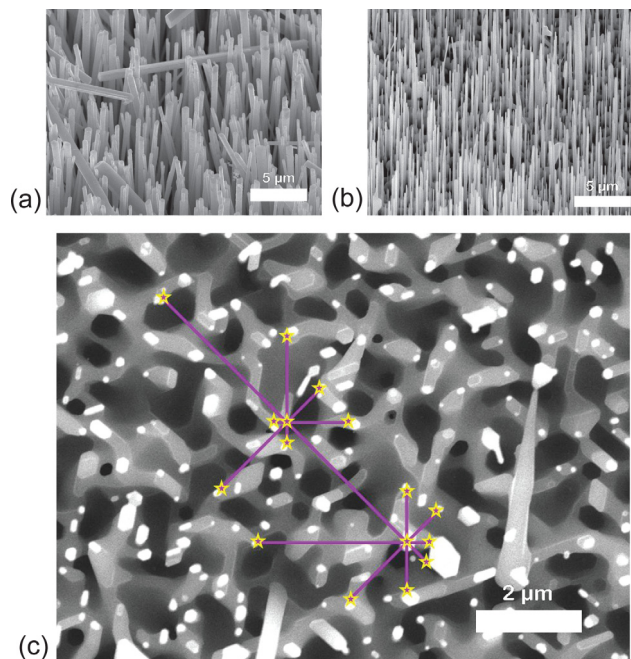


FIG. 1. (Color online) SEM images of the nanowire forests. (a) Nanowire forest 1. (b) Nanowire forest 2. (c) Top view of nanowire forest 2. Rays and scattering events are shown, indicating how we determined the photon mean free path from this image.

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the wire. The nanowire forests therefore consist of a nanowire part and a film part. The film is well visible in the top view image of forest 2 (Fig. 1(c)). The selected nanowire forests differ from each other with respect to nanowire length, diameter, and density. Properties of the samples are summarized in Table I.

Experimental results on nanowire forest 1 are shown in Fig. 2. Figure 2(a) shows the measured transmission of the probe pulse versus wavelength in the absence of a gating pulse. The transmitted light was diffusive; no beam was present behind the sample. The measured probe transmission in the presence of a gating pulse is presented in Fig. 2(b). Clearly, when the two pulses arrive approximately at the same time, the transmission of the probe pulse is reduced: the effect of two-color two-photon absorption. We also observe that the two-photon absorption dip is wider for shorter probe wavelengths, like in Ref. 22, which is explained by the smaller group velocity at wavelengths close to the exciton resonance in ZnO.

The sample of Ref. 22 is a $523\ \mu\text{m}$ thick single crystal, through which light propagates in a straight line, while here we have a $21.5\ \mu\text{m}$ thick nanowire forest, through which light propagates in a diffusive manner. If the photons would have traversed the forest in a straight line, then the two-photon absorption dip should be about $1/24$ of the widths measured in Ref. 22. The dips in Fig. 2(b) are, however, much wider, around 1 ps. This directly shows that diffusion severely lengthens the dwell time of the photons, which is in agreement with our direct observation that the transmitted light is diffusive. The dwell time of photons inside the nanowire forest apparently is in the order of 1 ps.

For further analysis of our experimental results, we used the following simple ray-optics diffusion model. Since the incoming gating and probe photons propagate parallel to the nanowires, initially scattering and diffusion are not very strong. There is waveguiding through the wires and propagation through the air between the wires. In our rough model, all photons travel ballistically to the center of the forest, where they scatter, and diffusion commences. The diffusion is modeled using standard diffusion theory²⁵ with an isotropic MFP for the nanowire part and a different isotropic MFP for the film part of the sample. We have set the boundary conditions such that a photon escapes as soon as it reaches the top surface of the forest or the interface between the porous film and the sapphire.

The photon MFP is estimated from the SEM images. It is assumed that whenever a photon hits a nanowire, it scatters with equal probability in all directions. From many nanowires on our SEM images we have drawn rays in eight directions, as indicated for two wires in Fig. 1(c). The photon MFP in the nanowire part equals the average distance to the

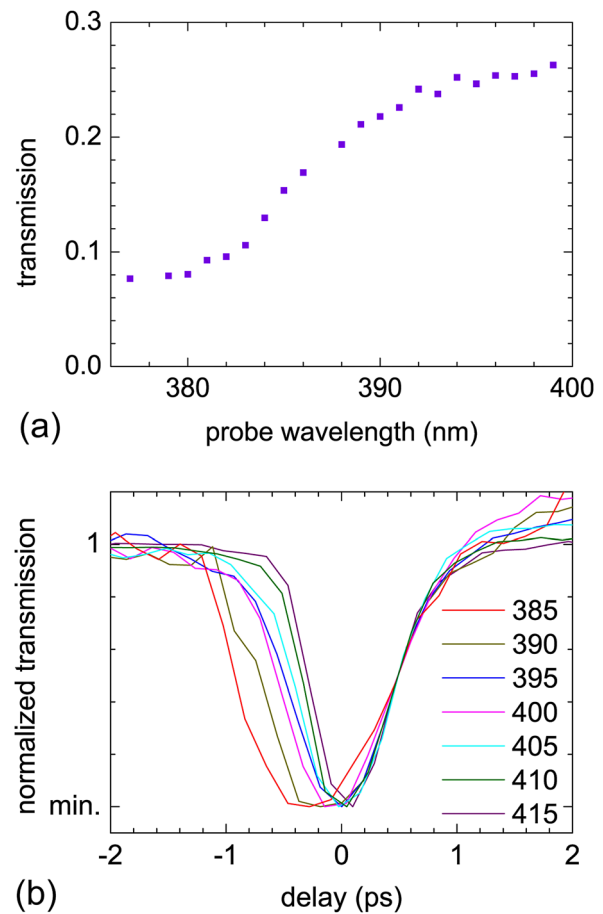


FIG. 2. (Color online) Experimental results on nanowire forest 1. (a) Absolute transmission. (b) Transmission of the probe pulse versus delay with respect to the gating pulse. Positive delay means that the probe pulse arrives after the gating pulse. Probe wavelengths are indicated in nm. The shape and width of the dip turned out to be independent of gating fluence. For clarity, the initial transmission level and the transmission minima are normalized. For shorter probe wavelengths the two-photon absorption dip is wider, revealing a longer dwell time of the probe photons inside the sample.

next nanowire determined in this way, multiplied by $\sqrt{2}$ to account for motion in the vertical direction. For the film part the MFP is estimated in a similar manner. The results are given in Table I. In this simple model, the MFP is taken to be independent of wavelength.

From the photon MFP the diffusion coefficient is calculated using $D = cl/[3n_{g\text{eff}}(\lambda)]$,²⁵ where c is the vacuum speed of light, l is the photon MFP, and $n_{g\text{eff}}$ is the wavelength-dependent effective group index of refraction, given by $n_{g\text{eff}}(\lambda) = n_{\text{eff}}(\lambda) - \lambda dn_{\text{eff}}(\lambda)/d\lambda$. Here, the effective index of refraction n_{eff} is determined from $n_{\text{eff}} = \text{Re}[\sqrt{\epsilon_{\text{eff}}(\lambda)}] = \text{Re}[\sqrt{f\epsilon_{\text{ZnO}}(\lambda) + (1-f)\epsilon_{\text{air}}}]$,^{26,27} where $\epsilon_{\text{ZnO}}(\lambda)$ is the complex dielectric constant of ZnO, ϵ_{air} is the dielectric constant of air, and f is the ZnO fraction, given in Table I. The

TABLE I. Properties of the samples examined in this work, determined from SEM images.

Sample	Nanowire length	Average diameter	Nanowire density	ZnO fraction nanowire part	Photon MFP nanowire part	Film thickness	ZnO fraction film part	Photon MFP film part
Nanowire forest 1	$20\ \mu\text{m}$	250 nm	$0.85\ \mu\text{m}^{-2}$	0.080	$5.9\ \mu\text{m}$	$1.5\ \mu\text{m}$	0.75	$0.54\ \mu\text{m}$
Nanowire forest 2	$7.6\ \mu\text{m}$	170 nm	$2.4\ \mu\text{m}^{-2}$	0.086	$2.1\ \mu\text{m}$	$1.5\ \mu\text{m}$	0.75	$0.54\ \mu\text{m}$

real part of the dielectric constant of ZnO is taken from Refs. 28–30 and the imaginary part from Ref. 31. Apart from diffusion, absorption also influences the dwell time of light inside the sample. We included in our model a linear absorption factor derived from the experimental data shown in Fig. 2(a). The effect of three-photon absorption of the 800-nm gating pulse on the dwell time is neglected as we do not observe any change in shape of the dip for increasing gating fluence and thus for increasing three-photon absorption.

Using our diffusion model, we calculated the functions $U(\lambda, t)$, defined as the wavelength- and time-dependent fraction of the pulse energy present as light inside the sample. The transmission versus delay δ of the probe with respect to the gate pulse can subsequently be calculated from

$$T(\lambda_{\text{probe}}, \delta) = 1 - c_1 \int_{-\infty}^{\infty} U(\lambda_{\text{probe}}, t - \delta) U(\lambda_{\text{gate}}, t) dt, \quad (1)$$

where c_1 is a constant. The integral describes the two-photon absorption of a probe photon and a gate photon. Results for forest 1 are presented in Fig. 3.

In Fig. 4 the two-photon dip widths of Fig. 3(b) are compared with the experimental dip widths of Fig. 2(b). On average, the dip width is well described by our simple diffusion

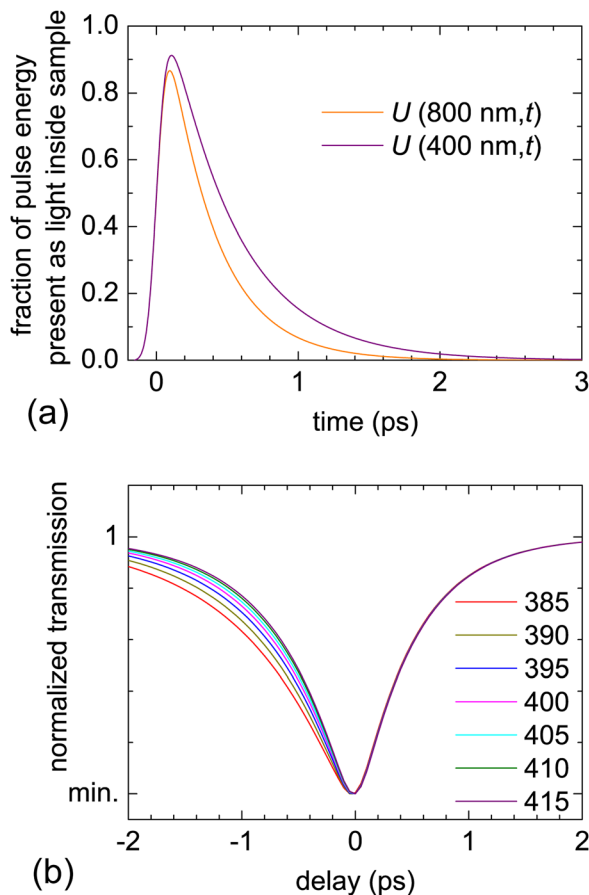


FIG. 3. (Color online) Results from our ray-optics diffusion model, with the photon MFP derived from the SEM images. (a) Dynamical fraction of the pulse energy present as light inside forest 1, calculated for an 800-nm pulse and for a 400-nm pulse. The increase is due to the incoming pulse. The decrease is due to two effects: photons leaving the sample and absorption. (b) Calculated transmission through forest 1 versus delay for various probe wavelengths, indicated in nm.

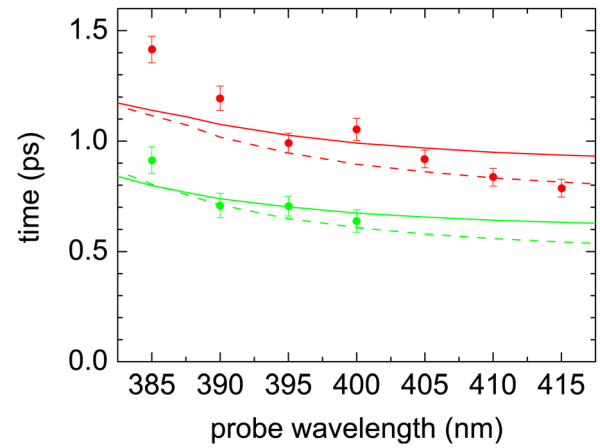


FIG. 4. (Color online) Comparison between diffusion model and optical shutter measurements. Red points: measured two-photon absorption dip width (full-width half-maximum) of forest 1 (Fig. 2(b)). Red solid line: dip width (full-width half-maximum) of forest 1 according to the diffusion model (Fig. 3(b)). Red dashed line: average time spent inside forest 1 by a probe photon as calculated from the diffusion model. Green points and lines: idem for forest 2.

model. Also for nanowire forest 2, the model dip widths reasonably agree with the measured ones. The dashed lines in Fig. 4 indicate the average photon dwell time in the two samples, which is simply given by

$$\bar{\tau}(\lambda) = \int_{-\infty}^{\infty} U(\lambda, t) dt. \quad (2)$$

As is clear from Fig. 4, the average dwell time is close to the dip width.

The model results show larger dip widths for shorter wavelengths, in agreement with the experimental data. This is the result of the higher group index of refraction and thus the smaller diffusion coefficient. The slopes in Fig. 4, however, deviate from the experimental results due to our rough approximation that the MFP is independent of wavelength. A more advanced model could take the wavelength-dependency into account. We wish to emphasize, however, that it is of practical use that a simple ray-optics model, in which the photon MFP is measured from SEM images, describes the light diffusion and the dwell times of light already reasonably well.

In conclusion, we have demonstrated a simple and straightforward method to measure the diffusive dwell time of light inside ZnO nanowire forests. This method is based on two-photon absorption of a gating photon and a probe photon. The diffusion can be reasonably well described by standard diffusion theory, in combination with a simple ray-optics model, where the photon MFP is determined from SEM images. We expect these results to be of value for nanowire solar cell research.

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