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Fundamental limits in the external quantum efficiency of single nanowire solar cells

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The fundamental limits for the measurement of the efficiency of single nanowire solar cell devices are presented. We evaluate the effect of the substrate, light polarization, and existence of Mie resonances in the absorption of the solar spectrum for nanowires with diameters from 10 to 300 nm. We find that the efficiency measured under such configuration can be underestimated between a factor 1.6 and 7.0 for GaAs nanowires and between 6.7 and 15.9 for silicon nanowires. These results constitute a reference for understanding the limits in the measurement of single nanowire devices. © *2011 American Institute of Physics*. [doi:10.1063/1.3672168]

Nanowires are filamentary crystals with a diameter in the order of few nanometers. Their increasing importance in both science and engineering is a consequence of the great number of fundamental experiments and applications they enable.[1–8] In the recent years, an increasing interest in the use of nanowires for solar cell applications has been observed.[9] The set point for this was the realization that radial nanowire p(i)n junctions offer a significant advantage with respect to the planar counterparts, as they allow to orthogonalize the light absorption with the carrier separation in the device.[10] Additionally, the possibility of combining lattice mismatched materials in one same device opens great perspectives in the area of multiple junction photovoltaics.[7,8,11,12] Recently nanowire based solar cells with both axial and radial p-n junctions have been demonstrated in various material systems.[13–16] Even though the ultimate device should consist in a forest of vertical nanowires, to date many experiments are carried out on single nanowire devices that are placed on a substrate with the light incident perpendicular to the substrate surface.[13,15,16] This geometry offers more flexibility for basic material characterization and is also promising for powering nanoelectronic devices.[17] However, it removes all advantages of the radial pn junction as light absorption and carrier separation are not orthogonal any more. Additionally, light absorption becomes diameter dependent and is strongly reduced. The measured efficiency represents a large underestimation of the value that could be obtained in a forest formed by the identical vertical nanowires.

The internal quantum efficiency (IQE) of a device corresponds to the efficiency of light conversion once the light has been absorbed in the device. The external quantum efficiency (EQE) refers to the one measured with respect to the incident light. In planar solar cells, an antireflecting treatment is incorporated so that the ratio EQE/IQE can be as close as 1 as possible. Several calculations and experimental results indicate that the ratio EQE/IQE can be nearly 1 for nanowire or nanocone arrays.[9,18,19] This is far to be the case for single nanowires. Several factors affect the absorption in a nanowire positioned on a substrate (Fig. 1(a)). It has been shown that light absorption can be significantly affected by the incident polarization and Mie scattering.[20,21] As a consequence, the cross-section of absorption can significantly deviate from the geometrically projected area of the nanowire on the substrate. This can cause substantial deviations between the measured EQE and the actual IQE. This is of extreme importance when trying to optimize the device by single nanowire measurements. Also, it shows that the comparison of the efficiency of single nanowire devices of different diameters and/or positioned on different substrates is not straightforward. While there has been a certain debate in literature on the magnitude of such deviations, it has been difficult to quantify and separate from other influences.[22]

In this letter we calculate the ratio EQE/IQE of single GaAs and Si nanowires positioned on a substrate. The calculations are realized for nanowires with diameters from 10 to 300 nm exhibiting a hexagonal cross-section. We compare the values for two different substrates: silicon dioxide and metal. The calculations consist of steady state electrodynamic simulations by the use of MEEP.[23] The structure of the 2D simulation area is sketched in Fig. 1(b). As boundary condition we choose perfectly matched absorbing layers to avoid any reflection with the borders. The hexagonal nanowire is placed on a semi infinite substrate with either $\epsilon = 1$ (no substrate), $\epsilon = 2.25$ (glass), or $\epsilon = -\infty$ (a perfectly reflecting electrical conductor). The illumination is performed using a plane wave

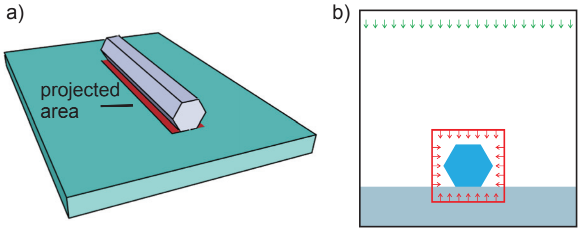

FIG. 1. (Color online) (a) Sketch of the simulated experimental condition of a hexagonal nanowire placed on a planar substrate and illuminated with a plane wave light perpendicular to the substrate surface. (b) Sketch of the 2D-simulation geometry. The net energy flux through a box around the nanowire (red arrows) is evaluated and normalized through the flux through the projected area of the nanowire on the substrate.

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incident from the top of the simulation area that is polarized either parallel or perpendicular to the nanowire axis. The calculations are performed for both single crystalline Si and GaAs nanowires using literature values for the wavelength dependent real and imaginary parts of the dielectric functions.[24] One should note that we only consider the absorption in intrinsic material and neglect changes in the absorption coefficient induced by doping. The nanowire absorption is obtained by calculating the net flux inside a box around the nanowire and normalized to the flux through the geometrically projected area of the nanowire on the substrate, as obtained from a reference simulation without nanowire and substrate. In this way we obtain the effective fraction of the flux incident on the nanowire. We perform separate simulations for light polarized parallel and perpendicular to the nanowire axis.

We start by showing the spectral and substrate dependence of absorption in a single nanowire with diameter of 80 nm (as measured by the distance of two opposite hexagonal faces). The ratio EQE/IQE for both a Si and GaAs nanowire is shown in Fig. 2. In the case of the silicon nanowires both without and with glass substrate, the total calculated absorption is less than 0.043 for photon energies up to 2 eV. This small value is consistent with the absorption length of silicon. Due to the indirect nature of the band gap this corresponds to several micrometers,[24] orders of magnitude larger than the nanowire diameter. For photon energies around 2.54 and 3.14 eV we observe an pronounced enhancement of absorption due the presence of resonant modes in the nanowire and a higher value of the coefficient of absorption. For these resonances the EQE/IQE ratio increases to 1.17 (0.73) and 0.99 (0.95) for the nanowire in air (on glass). The calculated spatial electromagnetic field energy distribution ($\sim E^* \cdot D + H^* \cdot B$) is plotted in the inset of Fig. 2. Interestingly the glass substrate dampens the Mie resonance in the nanowire and does not affect the position. This is quite different in the case of a perfectly reflecting metal substrate ($\epsilon = -\infty$) where the simulations show a blue shift of the resonances. A TM_{00} like resonance around 1.7 eV with a collection area of 0.54 appears. Meanwhile the TM_{01} resonance shifts to 2.2 eV with a EQE/IQE ratio over 2.2. The third resonance shows a slight blue shift to 3.2 eV with a peak absorption of 1.14.

As GaAs is a direct band-gap semiconductor, the EQE/IQE ratio in a 80 nm GaAs nanowire exceeds 0.25 for photon energies higher than 1.5 eV. The maximum absorption efficiencies for nanowires in air (1.75) and on glass substrate (1.45) is observed at 2.51 eV. The case on the perfectly reflecting metal surface shows a peak absorption efficiency as high as 3.43 for a photon energy of 1.71 eV. For photon energies above 2.9 eV the absorption efficiency saturates around ~1 for all three cases. This corresponds to the regime where the absorption length is significantly shorter than the diameter of the nanowire. Interestingly, the overall energy location of the resonances and the electromagnetic field energy distributions are quite comparable for both the Si and GaAs nanowires. This can be attributed to the quite small differences in the real part of the dielectric function of the two materials.

Now we turn our attention towards the total value of the EQE/IQE ratio in typical solar illumination conditions. We sum the weighted EQE/IQE ratio for energies between band gap (Si = 1.12 eV, GaAs = 1.42 eV) and 3.5 eV with respect to the incoming photon flux of an AM1.5 G solar spectrum. The resulting value corresponds to the fraction of photons with energy above the band-gap that generates an electron-hole pair. In Fig. 3 we show the AM1.5 G weighted EQE/IQE values for nanowire diameters in the range of 10-300 nm. The figure shows the EQE/IQE ratio of Si and GaAs nanowires for illumination with unpolarized light for the three considered substrate conditions.

For nanowire diameters above 150 nm the EQE/IQE for GaAs nanowires on glass under AM1.5 G spectral illumination is only in the oder of 0.5. This means that only about every second photon with energy above the band-gap is able to create an electron-hole pair in the nanowire. For silicon nanowires we obtain collection efficiencies between 0.048 and 0.13 within the entire range of diameters in Fig. 3. The

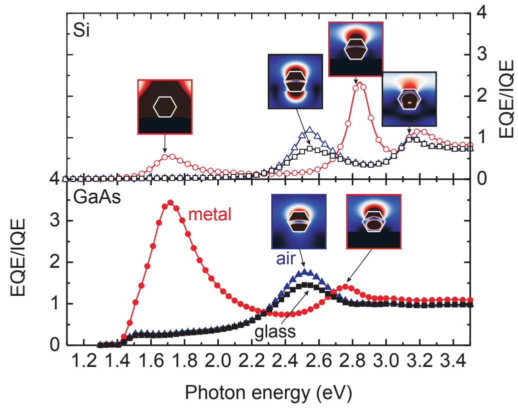

FIG. 2. (Color online) Ratio of external quantum efficiency to internal quantum efficiency (EQE/IQE) in dependence of photon energy for cases of nanowire in air (▲), on glass substrate (■) and on an ideally reflecting metal surface (●). The open symbols correspond to crystalline silicon nanowires while the filled symbols correspond to crystalline GaAs. The data shown corresponds to incident light polarized parallel to the nanowire axis and a wire diameter of 80 nm. The inset shows the calculated electric field energy distribution for selected data points indicated by the arrows.

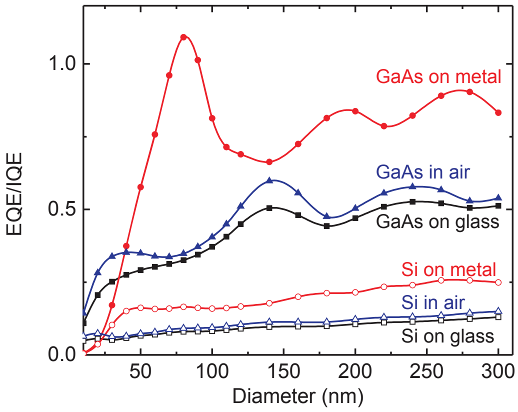

FIG. 3. (Color online) Photons absorbed in the nanowire normalized to the geometrically incident flux of photons of an AM1.5 G solar spectrum on the projected surface area. Only photons with an energy above the band-gap are considered. The data is shown in dependence of wire diameter for cases of nanowire in air (▲), on glass substrate (■) and on an ideally reflecting metal surface (●). The open symbols correspond to crystalline silicon nanowires while the filled symbols correspond to crystalline GaAs.

nanowires on glass substrates show a systematic slight decrease of collection efficiency compared to the nanowires in air. This can be understood that the dielectric substrate causes a slight damping for the case of Mie resonances but otherwise leaves the absorption unchanged. At the same time the ideally reflecting metal substrate ($\epsilon = -\infty$) shows an improvement of light absorption by a factor of ~1.5 (for GaAs) and ~1.7 (for Si) with respect to the case without any substrate. For the GaAs nanowire on the ideally reflecting substrate under illumination with an AM1.5 G spectra, the calculation yield a peak EQE/IQE of ~1.1. For this condition the nanowire will absorb more photons that what are geometrically incident to its projected surface area.

In typical experiments with single nanowire p(i)n junctions the conversion efficiency is calculated by normalizing the obtained solar power of the device to the incident solar power on the geometrically projected area. We have shown that for almost the entire range of experimental conditions the ratio EQE/IQE, and therefore the "effective" projected collection area is quite smaller than unity. As a consequence, the IQE could significantly deviate from the measured EQE. The results of Fig. 3 could act as a guideline for estimating a lower limit for the internal quantum efficiency of a single nanowire device from an experimentally obtained EQE.

In conclusion we have shown the influence of the configuration of single nanowire solar cells in the measurement of the conversion efficiency. The geometry used for nanowires mounted planar on a substrate can lead to the systematic measurement of lower values, which are a consequence of the reduced coupling of the incident light in the nanowire. The calculated EQE/IQE ratio for Si and GaAs nanowires illuminated by a AM1.5 G spectrum can be used as a reference for converting experimental efficiency values into the internal efficiency of the devices. This will enable a better comparison between the groups and materials systems.

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