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Nanoscale imaging of photocurrent enhancement by resonator array photovoltaic coatings

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Abstract

Nanoscale surface patterning commonly used to increase absorption of solar cells can adversely impact the open-circuit voltage due to increased surface area and recombination. Here, we demonstrate absorptivity and photocurrent enhancement using silicon dioxide (SiO₂) nanosphere arrays on a gallium arsenide (GaAs) solar cell that do not require direct surface patterning. Due to the combined effects of thin-film interference and whispering gallery-like resonances within nanosphere arrays, there is more than 20 % enhancement in both absorptivity and photocurrent. To determine the effect of the resonance coupling between nanospheres, we perform a scanning photocurrent microscopy (SPCM) based on a near-field scanning optical microscopy (NSOM) measurement and find a substantial local photocurrent enhancement. The nanosphere-based antireflection coating (ARC), made by the Meyer rod rolling technique, is a scalable and a room-temperature process; and, can replace the conventional thin-film-based ARCs requiring expensive high-temperature vacuum deposition.

Keywords

Antireflection coatings (ARCs); whispering gallery modes; absorptivity enhancements; photocurrent enhancements; near-field scanning optical microscopy (NSOM)

1. Introduction

Global climate change fuels the demand for renewable, earth abundant and environmentally friendly energy sources. Solar energy harvesting is a strong candidate to address a wide variety of societal issues, and improving the performance of solar cells has become an important challenge. To boost the efficiency of solar cells, short-circuit current and/or open-circuit voltage should be increased. Short-circuit current can be enhanced through improved light absorption within the active material of solar cells. Traditionally, either single or multiple layers of dielectric thin-film antireflection coatings have been used for high absorptive solar cells.^{1–3} However, for more efficient and lower cost devices, innovative schemes for better light trapping with micro- and nanoscale surface patterning have been

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proposed, producing tangible results. Research using nanocones,^{4–6} nanopyramids,⁷ black silicon,^{8–10} etc., shows significant improvement of light absorption within solar cells. However, the increased surface area derived from the surface patterned nanostructures may cause an undesired recombination losses and the respective decrease of the open-circuit voltage, thus limiting these approaches in improving the total power conversion efficiency.

Alternatively, absorptivity enhancement based on plasmonic nanostructures,^{11–18} dielectric micro- and nanostructures,^{19–24} or Mie resonators^{25–28} has been explored as a pathway to increase light absorption within solar cells without the loss of the open-circuit voltage. Such structures can be deposited on substrates without direct transformations of the active material of solar cells and can potentially be directly employed on semiconductors to make high-efficiency solar cells. However, for practical application the costs of fabrication, abundance of materials and environmental impact (e.g., recycling ability) need to be taken into consideration. A recent example of an environmentally friendly and cost-effective light management technique is based on cellulose fibers.^{29–31} A significant absorptivity enhancement without a loss in the open-circuit voltage has been observed due to texturing of cellulose fibers and gradual change of the refractive index from air to the active material, which in turn brought $\approx 24\%$ enhancement in the power conversion efficiency of GaAs solar cells.³⁰

Another promising approach to increase light absorption in solar cells is based on exciting and coupling to optical resonance modes using spherical resonators.^{21–24,32,33} The incident light is coupled into the spherical resonators from a wide solid angle exciting whispering gallery-like modes, with the name originating from the acoustic wave resonances in the St. Paul's cathedral in London explained by Rayleigh.³⁴ Being mainly surface modes, photonic whispering gallery excitation ultimately leads to increased light absorption within the high index active material of solar cells located below the resonators. Among multiple candidate materials for spherical resonators, dielectric nanospheres have received a lot of attention. With the dielectric nanospheres, there is an additional effect due to the gradual change of the refractive indices from air to the high index of the active material of the solar cell, further enhancing absorption. Close-packed arrays of nanospheres required for high surface coverage can potentially enable better coupling of the resonators.^{21–24,32,33,35–40} To construct monolayer close-packed nanosphere arrays, many approaches have been used including the Langmuir-Blodgett method,^{23,41} sedimentation,^{42,43} evaporation,^{44,45} and the Meyer rod rolling technique.^{24,46} For practical application as an antireflective coating for commercial photovoltaics, the deposition process has to be inexpensive and compatible with continuous production.

The evaluation and the optimization of dielectric nanosphere arrays have been mainly based on numerical calculations.^{21,22} However, far-field experimental measurements have demonstrated limited agreement with the simulations.^{23,24} In this paper, we bridge the gap between the nanoscale and the macroscale experiments and calculations. We demonstrate that a scalable ARC based on SiO₂ dielectric nanosphere arrays can improve optoelectronic properties of solar cells based on GaAs. The close-packed configuration of those resonators leads to the excitation of various optical modes including thin-film interference effects and whispering gallery-like modes, which ultimately lead to improved optoelectronic properties

of the solar cells. We also show that excited optical resonances can be tuned depending on size and/or configuration of nanosphere arrays. For nanoscale measurements, near-field scanning optical microscopy (NSOM) is used to characterize the interaction between the nanosphere arrays and a solar cell. NSOM measurements exploit evanescent waves enabling high spatial resolution below the diffraction limit. In our experiment, we use a tapered fiber coated by metal with small openings in the metal coating mounted on a tuning fork-based non-contact mode atomic force microscopy (AFM) probe to locally inject light and measure photocurrent generated by a solar cell.^{47,48}

2. Results and Discussion

We present a scalable ARC for photovoltaics using SiO₂ nanosphere arrays atop a GaAs solar cell, which enables broadband and narrowband enhancements in absorptivity and photocurrent of the solar cell. As a deposition method, we employ the Meyer rod rolling technique (see Fig. S1 in the Supplementary Information for more details). By rolling the Meyer rod across a flat substrate, the water-based SiO₂ nanosphere suspension is spread, and a monolayer of SiO₂ nanosphere arrays is made. By adjusting either the size of the Meyer rod or the concentration of the SiO₂ nanosphere suspension, the surface coverage and/or the number of deposited layers can be precisely controlled with high reproducibility.⁴⁶ As this process is based on rod rolling technique, it can be potentially compatible with high-speed roll-to-roll process enabling low-cost and high speed fabrication of antireflection coatings. Scanning electron microscope (SEM) image in the inset to Fig. 1a shows a representative 700 nm SiO₂ nanospheres array on a GaAs solar cell coated with the Meyer rod rolling technique. In real operational environments, the deposited SiO₂ nanospheres should be covered with encapsulation layers (e.g., glass protection layers) for protection from outdoor environmental factors (e.g., dust, water condensation, wind, etc). The encapsulation layer could be placed far above from the nanospheres, e.g., using spacers, to guarantee the appropriate optical couplings to solar cell substrate.

To understand how SiO₂ dielectric nanosphere arrays affect the optical properties of a GaAs solar cell, we determine the absorptivity enhancements within the active material (GaAs) from macroscale optical measurements and compare these results with finite-difference time-domain (FDTD) calculations. To determine the absorptivity enhancements, absorptivity with nanosphere arrays is normalized to that of a bare GaAs solar cell. Measurements are made as a function of wavelength ($\lambda = 450$ nm to 860 nm) and incident angle ($\theta = 10^\circ$ to 55°) using monochromatic light and an integrating sphere. Monochromatic light is incident on a GaAs solar cell placed at the center of the integrating sphere. For FDTD calculations, we assume a close-packed array of 700 nm SiO₂ nanospheres on a GaAs substrate. As the light source is unpolarized, the calculations are made for both incident polarizations and averaged to match the experimental data over the range of wavelengths ($\lambda = 450$ nm to 860 nm) and incident angles ($\theta = 0^\circ$ to 55°) of interest (see Fig. S2 in the Supplementary Information for more details). A plane wave source is used for the calculations. To reduce the simulation time, we use periodic boundary conditions in the directions parallel to the interface between nanosphere arrays and the GaAs substrate when light is at normal incidence (or Bloch boundary condition at non-normal incidence). Also, a perfectly matched layer boundary condition is applied to the top and bottom of the simulation volume.

Refractive indices for the materials are adopted from the Ref. 49 (see the Experimental Methods for more details). Note that the measurements are performed for incident angles larger than 10° while the angles in the FDTD calculations start from the normal incidence. Due to the geometrical constraints of the integrating sphere, the minimum measurable incident angle should be greater than 8° . Both measurements and calculations are performed at a step of 5° that is sufficient to follow the overall trends, especially in the case of macroscale measurements.

The absorptivity enhancements shown in Fig. 1a (measured) and Fig. 1b (calculated) are observed over the entire visible spectrum. In addition, the narrowband absorptivity enhancements over the various wavelengths and incident angles are seen in Fig. 1b. The broadband enhancements occur at wavelengths of ≈ 500 nm and ≈ 670 nm at normal incidence and then gradually shift to shorter wavelengths as the incident angle increases. We attribute the origin of these broadband enhancements to an antireflective effect due to thin-film interference. To show this effect, we model the array as a thin-film with a thickness equal to the diameter of a SiO_2 nanosphere and with an effective refractive index varying through the thickness resulting from a weighted average – *i.e.*, the refractive index near the top and bottom of nanosphere arrays converges to that of air ($n = 1$) and that at the center of the nanosphere arrays converges to that of SiO_2 ($n = 1.5$). The weighted-average is determined by the geometric fraction of SiO_2 and air (the index variation is depicted in the inset above Fig. 1c). As shown in Fig. 1c, the absorptivity enhancements from the thin-film calculation model qualitatively explain the broadband absorptivity enhancements of SiO_2 nanosphere array observed in macroscale experiments (Fig. 1a) and FDTD calculations (Fig. 1b) very well. However, the experimentally observed enhancement is larger than the prediction of this simplified model, and the narrowband absorptivity enhancements clearly seen in the FDTD calculations (Fig. 1b) are not accounted for in this simple model. The difference is significant: at normal incidence, the light absorption averaged over the entire operational spectrum of a GaAs solar cell is enhanced by $\approx 4\%$ in the simplified model, while the enhancement generated by 700 nm close-packed nanosphere array calculated in Fig. 1b and counting all narrowband and broadband features is significantly larger, $\approx 12.5\%$.

To understand the physical origin of the narrowband absorptivity enhancements shown in Fig. 1b, we analyze electric field intensity profiles at the corresponding wavelengths. Narrowband absorptivity enhancement peaks occur at wavelengths of 635 nm and 798 nm at normal incidence. Figure 1d shows electric field intensity profiles at resonances ($\lambda = 635$ nm and $\lambda = 798$ nm, number 1 and 2, respectively) and off-resonance ($\lambda = 850$ nm, number 3) in Fig. 1b. Electric field intensity profiles within the nanospheres under transverse electric (TE) and transverse magnetic (TM) incident polarizations are shown for each wavelength as well as the lateral electric field intensity profiles at the interface between the SiO_2 nanosphere array and the GaAs substrate. Strong electric fields around the shell of nanospheres are observed at resonances ($\lambda = 635$ nm and $\lambda = 798$ nm, number 1 and 2, respectively) under TM incident polarization resembling the electric field profiles of excited whispering gallery modes of an isolated nanosphere.²² A conventional whispering gallery mode exists in a spherical resonator surrounded by a uniform medium.^{35–39} This conventional whispering gallery mode, an electromagnetic mode with azimuthal variations,

can be classified as either TE or TM mode depending on the field in the radial direction. However, once spherical resonators are placed in a close proximity to each other and to a solar cell, the pure whispering gallery mode no longer exists. First, the resonators are coupled to the solar cell whose refractive index differs from that of the surrounding material, usually air. Second, the spherical resonators are coupled to the neighboring resonators within the array. Therefore, we refer to the excited resonance modes as whispering gallery-like modes rather than pure whispering gallery modes. Lateral electric field intensities are enhanced at the interface between SiO₂ nanosphere array and the GaAs substrate when whispering gallery-like modes are excited bringing about the narrowband absorptivity peaks (compare resonances marked with number 1 and 2, at 635 nm and 798 nm, respectively, to off-resonance marked with number 3 in Fig. 1d). These modes do not exist in the simplified thin-film model shown in Fig. 1c.

Having demonstrated the absorptivity enhancements with the SiO₂ nanosphere arrays-based ARC from optical calculations and experiments (Fig. 1), we also determine how this ARC affects electrical properties of solar cells. First, we determine the angle-dependent current density of a GaAs solar cell with close-packed 700 nm SiO₂ nanospheres under AM1.5G conditions. Investigation of angular dependence of an ARC is critical for photovoltaic applications without mechanical solar trackers. For simplicity, we assume that the solar cell has a perfect internal quantum efficiency (IQE). The IQE of the solar cell is defined as:

$$\eta_{IQE}(\lambda) = \frac{\eta_{EQE}(\lambda)}{A(\lambda)}$$

where $\eta_{EQE}(\lambda)$ is the external quantum efficiency (EQE), $\eta_{IQE}(\lambda)$ is the internal quantum efficiency of the solar cell, and $A(\lambda)$ is the absorptivity within the absorbing material of the solar cell, a GaAs substrate. As we assume perfect IQE of our cell, the EQE of the solar cell equals to the absorptivity of the GaAs substrate, and then the solar spectrum-weighted current density can be determined from the following expression:

$$J_{AM1.5G} = \int_{\lambda_s}^{\lambda_{Eg}} q \cdot S(\lambda) \cdot \eta_{EQE}(\lambda) d\lambda$$

where $J_{AM1.5G}$ is the AM1.5G solar spectrum-weighted photocurrent density, λ_{Eg} is the wavelength corresponding to the bandgap of the absorbing material ($\lambda_{Eg} = 870$ nm for GaAs), λ_s is the shortest wavelength in our calculation ($\lambda_s = 400$ nm), q is the charge of an electron, $S(\lambda)$ is the spectral irradiance of AM1.5G solar spectrum, and $\eta_{EQE}(\lambda)$ is the external quantum efficiency of the GaAs solar cell. Figure 2a shows calculated AM1.5G solar spectrum-weighted current density of a GaAs solar cell as a function of incident angle. For both incident polarizations (TE and TM), the current density has strong angular dependency. However, the averaged current density between two incident polarizations shows substantial improvements compared to a bare GaAs solar cell even at steep incident angles. The wide-angle acceptance of this ARC gives promise of future applications to commercial photovoltaics. We also determine the EQE of the GaAs solar cell with and

without the addition of SiO₂ nanosphere arrays (Fig. 2b). With the SiO₂ nanospheres, improved EQE is observed over the entire wavelengths where the measurement is made ($\lambda = 450$ nm to 890 nm). Broadband absorptivity enhancements observed at wavelengths of ≈ 500 nm and ≈ 670 nm in Fig. 1 improve the number of photo-generated electron-hole pairs in the GaAs solar cell, and the measured EQE also confirms the broadband enhanced features at those wavelengths. However, as in macroscale optical measurements (Fig. 1a), narrowband features are not clearly seen in the EQE measurement. We attribute the lack of narrowband features to the size distribution of nanospheres ($697 \text{ nm} \pm 82 \text{ nm}$) (see Fig. S3 in the Supplementary Information for more details). The non-uniform nanosphere arrays result in a broadening of the narrowband peaks into smaller but broader features, finally incorporated into broadband peaks.

To investigate the effect of non-uniformity of nanosphere arrays, we calculate absorptivity from seven different nanosphere arrays having variation in nanosphere size (see Fig. S4 in the Supplementary Information for more details). By averaging results from seven different configurations, the absorptivity of a quasi-non-uniform array is calculated. The size distribution in this quasi-non-uniform array mimics the size distribution obtained from the sample shown in Fig. S3. Compared to the absorptivity from close-packed 700 nm nanosphere arrays, the narrowband peaks become smaller but broader due to an averaging effect. This quasi-non-uniform model constructed with limited number of nanospheres cannot fully represent the non-uniformity of nanosphere arrays in the real sample. While accurate FDTD modelling of the non-uniformity of nanosphere arrays is prohibitively taxing, we evaluate the effect of non-uniformity on the achievable enhancements in a simplified model (Fig. 3). First, we calculate absorptivity of a GaAs solar cell with close-packed equal-size nanospheres with different diameters (from 630 nm to 770 nm). The narrowband absorptivity peaks are red-shifted as the diameter increases. To account for the size distribution of the real sample analyzed in Fig. S3, we calculate an averaged absorptivity weighted accordingly to the measured size distribution. It turns out that the non-uniformity of diameters in the real sample smears the narrowband peaks merging these into broadband features leading to a qualitative agreement with the macroscale optical and electrical measurements (see Fig. 1a and Fig. 2b). In Fig. 3, we also account for the incomplete surface coverage of the real sample (70 %) averaging the contributions of the ARC area (70 %) and of the bare GaAs (30 %). Despite the spectral spreading, the absorptivity of a non-uniform nanosphere arrays with 100 % surface coverage averaged over the spectrum is nearly equal to that obtained with close-packed 700 nm SiO₂ nanosphere arrays, which shows the conservation of total absorptivity enhancements (see Table 1 for more details).

While the developed models appear to capture the main features of the macroscale measurements, there has been no direct experimental proof of the narrowband effects and, therefore, the adequacy of the modelling. To fully establish the validity of the model and its limitations, we investigate the photocurrent enhancements on different length scales, from an individual nanosphere to a scale where the narrowband enhancements smear out. To observe the nanoscale photocurrent enhancements generated by individual nanospheres, we perform a scanning photocurrent microscopy (SPCM) based on a near-field scanning optical microscopy (NSOM) technique. We use a tuning fork-based atomic force microscopy

(AFM) probe with an attached tapered fiber having an output hole with a diameter of 200 nm in the metal coating (see Fig. S5 in the Supplementary Information for more details). It operates in a non-contact mode with a center frequency of 34.85 kHz and a quality factor of ≈ 840 (see the Experimental Method for more details). To observe local photocurrent enhancements, we perform photocurrent imaging both at a wavelength of 635 nm (number 1 in Fig. 1b and d) corresponding to the whispering gallery-like mode excitation and at an off-resonance wavelength of 850 nm (number 3 in Fig. 1b and d). Nanoscale scanning is taken over the sample area marked with a white solid box in the SEM image in Fig. 4a. Figure 4b, c and d show the corresponding AFM topography and the local photocurrent imaging in this region at the wavelength of 635 nm and 850 nm, respectively. The photocurrent is normalized to that of the bare GaAs region. We observe a significant local photocurrent enhancement up to $\approx 30\%$ at a wavelength of 635 nm when illuminating the SiO₂ nanospheres and no enhancement at a wavelength of 850 nm, in agreement with the FDTD calculations in Fig. 1. Interestingly, the photocurrent peaks for tip illumination over the centers of each nanosphere, in agreement with previous studies of metallic nanoparticles using NSOM⁵⁰; however, the values of the enhancement vary. This variation is attributed to differences in nanosphere sizes and arrangement. Nanospheres with a diameter of ≈ 700 nm support whispering gallery-like modes at the wavelength of 635 nm, while the resonance coupling is weakened as the diameter deviates from 700 nm. Figure 4e and f show electric field intensity profiles at the interface between a 700 nm SiO₂ nanosphere and the GaAs substrate obtained from FDTD calculations. To model the NSOM illumination, we use a point dipole source at the top of the SiO₂ nanosphere (see the Experimental Methods for more details). White-dotted lines represent the circumference of the 700 nm SiO₂ nanosphere. Electric field intensity profiles in Fig. 4e ($\lambda = 635$ nm, number 1 in Fig. 1b and d) and f ($\lambda = 850$ nm, off-resonance, number 3 in Fig. 1b and d) qualitatively agree with the photocurrent enhancements in Fig. 4c ($\lambda = 635$ nm) and d ($\lambda = 850$ nm). The strong variation of the individual nanosphere enhancement at a particular wavelength seen in Fig. 4c suggests that the size non-uniformity is a significant factor broadening and reducing the resonances and their corresponding narrowband enhancements in the far-field measurements shown in Fig. 1a and Fig. 2b.

To investigate the effect of the non-uniformity at the scale of several close-packed neighboring resonators, we perform spectrally-resolved photocurrent measurement in a region of locally close-packed SiO₂ nanospheres using a fiber with a larger aperture, $\approx 1\ \mu\text{m}$, in the same NSOM setup. The NSOM probe is positioned over the SiO₂ nanospheres shown in the inset of Fig. 5. The fiber is coupled to a tunable laser with a 10 Hz repetition rate enabling the measurements over the wavelengths of interest ($\lambda = 450$ nm to 860 nm). The measured photocurrent is normalized to the incident power of the tunable laser at each wavelength to minimize the effects of power fluctuations in the laser, and the photocurrent measured on SiO₂ nanospheres is normalized to that measured on a bare region. Two broad maxima corresponding to the bands at wavelengths of ≈ 500 nm and ≈ 670 nm in Fig. 1a, b, and Fig. 2b are observed in photocurrent measurement in Fig. 5. At the wavelength of 635 nm corresponding to the excitation of a whispering gallery-like mode (number 1 in Fig. 1b and d), local photocurrent enhancement is $\approx 13\%$. This value of the enhancement is smaller than the one predicted in Fig. 1b due to the variation in the diameter of neighboring

nanospheres with the enhancement peak becoming broader. We also observe another resonant peak originated from the whispering gallery-like mode at a wavelength of 794 nm (number 2 in Fig. 1b and d), which is slightly off the calculation in Fig. 1 ($\lambda = 798$ nm). At a wavelength of 850 nm (off-resonance, number 3 in Fig. 1b and d) where no absorptivity enhancement is observed, no photocurrent enhancement is seen in the local measurements, as expected.

3. Conclusion

In conclusion, we present antireflection coatings based on dielectric nanosphere arrays that improve the optoelectronic properties of solar cells due to excitation of various optical resonances. The physical origin of the enhancements is revealed through the macro- and nanoscale measurements and FDTD calculations. We show that the combined effect of the thin-film interference and the whispering gallery-like modes leads to absorptivity enhancements more than 20 %. Using nanoscale NSOM measurements, we image photocurrent enhancements induced by resonator arrays and investigate the effects of the resonance coupling among SiO₂ nanospheres. As such an ARC can be made without a direct surface patterning, it is an excellent candidate to increase the power conversion efficiency of solar cells without the loss of the open-circuit voltage. Furthermore, because this ARC based on earth abundant and renewable materials can be made with easy and scalable processes, it can replace conventional thin-film-based ARCs requiring complicated, expensive, and high-temperature vacuum processes.

4. Methods Section

SiO₂ nanosphere coating on a GaAs solar cell:

To deposit a monolayer of SiO₂ nanospheres on a GaAs solar cell, the Meyer rod rolling technique is employed. The SiO₂ nanosphere suspension with a concentration of ≈ 0.1 % is spread onto a GaAs surface by rolling a wire wound Meyer rod. To prevent agglomeration of nanospheres, a surfactant is added into the SiO₂ suspension. A mild annealing at 50 °C for 1 min is used to evaporate solution.

Macroscale optical measurements:

Macroscale optical measurements are conducted based on a lock-in technique using a monochromatic light (a 150 W xenon arc lamp) with a monochromator, a 15.24 cm integrating sphere, and relevant optics.^{30,31} Absorptivity is determined from the measured reflectivity. The measurements are performed for incident angles larger than 10° due to the geometrical constraints of the integrating sphere. The spot size of incident light for absorptivity measurements is ≈ 0.5 cm². Repeated readings under identical conditions yielded maximum measurement variation less than 1 %.

Macroscale electrical measurements:

Two measurements are performed to determine EQE of a solar cell. First, we measure the incident power arriving at the measurement stage with a silicon (Si) photodetector. By calibrating the measured photocurrent of the photodetector with a known responsivity, total

number of incident photons for each wavelength at the measurement stage is determined. Then, we measure the photocurrent of the solar cell under the same measurement arrangement to determine the number of photo-generated electron-hole pairs within the device. EQE of the cell is determined by comparing the ratio between the number of photo-generated electron-hole pairs and the number of total incident photons for each wavelength. The spot size of incident light for EQE measurements is $\approx 0.2 \text{ cm}^2$. Repeated readings under identical conditions yielded maximum measurement variation less than 1 %.

FDTD calculations:

The FDTD method is used to determine the optical response of a GaAs substrate with and without SiO_2 nanosphere arrays. To model macroscale optical experiments, we use a plane wave source. A close-packed array of SiO_2 nanospheres is defined on top of a GaAs substrate, and the absorptivity within the substrate is determined from the simulated reflection from the structure. To reduce the simulation time, periodic boundary conditions are applied laterally for normal incidence. Bloch boundary conditions are applied when the incident plane wave is at a finite angle with respect to the normal. A perfectly matched layer boundary condition is applied at the top and bottom boundary of the simulation structure. To model nanoscale NSOM measurements, we apply a point dipole source in FDTD calculation. For this calculation, three different simulations are performed for three orthogonal direction of the dipole. The electric fields from each simulation are then added incoherently.

Photocurrent imaging:

We employ a near-field scanning optical microscopy (NSOM) measurement technique to demonstrate photocurrent enhancements resulting from excitation of resonances with a SiO_2 nanosphere array atop a GaAs solar cell. The NSOM probe having an output hole with a diameter of 200 nm cladded with 20 nm Cr followed by 200 nm Au coating is attached to a tuning fork-based atomic force microscopy (AFM) probe and is used for local light injection. The sample is placed onto a piezo stage, and topography and photocurrent are acquired at the same time while the NSOM probe makes a raster scanning. The probe operates with a force constant of 15 N/m and a resonance frequency of $\approx 35 \text{ kHz}$. A variable-gain low-noise current amplifier with a gain of 10^9 V/A is used to amplify the measured photocurrent signal. The distance between the NSOM probe and the top surface of the sample remains $\approx 10 \text{ nm}$ during the scanning.

Spectrally-resolved near-field photocurrent measurement:

Wavelength-dependent photocurrent is measured on a GaAs solar cell at the wavelengths of interest ($\lambda = 450 \text{ nm}$ to 860 nm). To incorporate effects from the coupling of neighboring SiO_2 nanospheres, a relatively large size ($1 \mu\text{m}$) NSOM probe is used. As a light source, a tunable laser with a 10 Hz repetition rate is coupled into an optical fiber connected to the NSOM probe. Because the tunable laser has a wavelength-dependent power, measured photocurrent is normalized to the incident laser power for each wavelength. Photocurrent of the GaAs solar cell is measured through the macroscopic contacts with the NSOM probe positioned at one location. The photocurrent enhancement is determined by normalizing measured photocurrent from the GaAs solar cell with SiO_2 nanosphere arrays to that from a

bare region. Repeated readings under identical conditions yielded maximum measurement variation less than 2 %.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Optical properties of a GaAs solar cell with SiO₂ nanosphere arrays. (a) Measured and (b) calculated absorptivity enhancements (A_E) as a function of wavelength ($\lambda = 450$ nm to 860 nm) and incident angle ($\theta = 10^\circ$ to 55° for measurements and $\theta = 0^\circ$ to 55° for calculations) with a monolayer of 700 nm SiO₂ nanospheres atop a GaAs solar cell. (c) Absorptivity enhancements calculated with an effective thin-film model that describes the broadband enhancements in (a) and (b). Inset to (a): SEM image shows a representative area of a GaAs sample coated with SiO₂ nanosphere array. Scale bar in the SEM image is 2 μ m. Top schematics (not to scale) above (a), (b), and (c) depict the cell structure. (d) Normalized electric field intensity profiles ($|E|^2$) at wavelengths corresponding to excited whispering gallery-like modes ($\lambda = 635$ nm, number 1 in (b) and $\lambda = 798$ nm, number 2 in (b)) and off-resonance illumination ($\lambda = 850$ nm, number 3 in (b)) at normal incidence ($\theta = 0^\circ$). Dotted lines indicate 700 nm SiO₂ nanospheres on a GaAs substrate, and solid lines indicate the interface between SiO₂ nanospheres and the GaAs substrate. Lateral electric field intensity profiles at the top of the GaAs substrate at resonances confirm the increased absorption due to the excitation of the resonances. Scale bars in (d) are 250 nm.

Figure 2.

Electrical properties of a GaAs solar cell with SiO₂ nanosphere arrays. (a) Angle-dependent current densities with and without SiO₂ nanospheres. Inset schematic shows the direction of two incident polarizations at normal incidence when light is traveling onto the surface of a GaAs solar cell. Angle of incidence (θ) is defined as the angle between an incident light on a GaAs solar cell and the line perpendicular to the surface of the GaAs solar cell at the point of light incidence. (b) Macroscopically determined external quantum efficiencies of a GaAs solar cell with and without SiO₂ nanospheres at normal incidence.

Figure 3.

(a) Calculated absorptivity with close-packed equal-size nanospheres having diameters from 630 nm to 770 nm (gray-dotted lines for all diameters except for a diameter of 700 nm represented with a bold gray-dotted line) suggests strong excitation of resonance modes. Calculated absorptivity of quasi-non-uniform nanosphere arrays (orange-dotted line) at 100 % surface coverage. Narrowband features are partly smeared. Calculated absorptivity weighted accordingly to the measured distribution of diameters at the surface coverage of 70 % (red-dotted line) and 100 % (blue-dotted line). Black-dotted line shows the absorptivity of a bare GaAs solar cell. All calculations are made at normal incidence with a plane wave source.

Figure 4.

Nanoscale photocurrent imaging based on an NSOM measurement technique, which demonstrate the photocurrent enhancements (I_E) resulting from the excitation of whispering gallery-like resonances. (a) SEM image shows the scanned area of the sample where the NSOM measurement is taken. (b) The AFM topography of the scanned area of the sample. Image of photocurrent enhancements at (c) whispering gallery-like mode excitation ($\lambda = 635$ nm, number 1 in Fig. 1) and (d) off-resonance ($\lambda = 850$ nm, number 3 in Fig. 1). Diameters of numbered nanospheres in (a) are as follows: ≈ 700 nm, 750 nm, 700 nm, 730 nm, 750 nm, 750 nm, from 1 to 6, respectively. FDTD-calculated normalized electric field intensity profiles ($|E|^2$) at an interface between a SiO_2 nanosphere and a GaAs substrate at (e) whispering gallery-like mode excitation ($\lambda = 635$ nm, number 1 in Fig. 1) and (f) off-

resonance ($\lambda = 850$ nm, number 3 in Fig. 1). In FDTD calculations, to mimic the NSOM illumination, a point dipole source is used atop the SiO₂ nanosphere. White-dotted lines represent the circumference of the 700 nm SiO₂ nanosphere. All scale bars are 500 nm.

Figure 5.

Local measurement of photocurrent enhancement by 700 nm SiO_2 nanosphere arrays atop a GaAs solar cell over the wavelengths of interest ($\lambda = 450 \text{ nm}$ to 860 nm). Enhancement is determined by normalizing measured photocurrent of the GaAs solar cell with the SiO_2 nanosphere array to the measured photocurrent of a bare cell. The close-packed SiO_2 nanosphere patch where the measurement is conducted is marked with a white-dotted circle in the SEM image (inset). Scale bar is $2 \mu\text{m}$. Light from a tunable laser is injected via an optical fiber attached to an NSOM probe, and measurement is taken while the NSOM probe is positioned atop the white-dotted circle. Inset schematic (not to scale) describes how the measurement is made. In the data, both broadband and narrowband enhancements are observed. Resonances (number 1 and 2 in Fig. 1 and Fig. 4) and off-resonance (number 3 in Fig. 1 and Fig. 4) are marked correspondingly, as is the broadband enhancement feature that is similar to the effect of a thin-film ARC.

Table 1.

Averaged absorption over the entire spectrum.

ARC Structure	Averaged absorptivity ($\lambda = 400$ nm to 860 nm)
Bare GaAs	63.06 %
Close-packed 640 nm SiO ₂ nanospheres atop GaAs	69.34 %
Close-packed 660 nm SiO ₂ nanospheres atop GaAs	69.78 %
Close-packed 680 nm SiO ₂ nanospheres atop GaAs	70.29 %
Close-packed 700 nm SiO ₂ nanospheres atop GaAs	70.96 %
Close-packed 720 nm SiO ₂ nanospheres atop GaAs	71.69 %
Close-packed 740 nm SiO ₂ nanospheres atop GaAs	72.25 %
Close-packed 760 nm SiO ₂ nanospheres atop GaAs	72.05 %
Quasi-non-uniform array with 100 % coverage	72.33 %
Weighted-average with 100 % coverage	70.96 %
Weighted-average with 70 % coverage	68.59 %