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ABSTRACT

We present a lossless, strong forward-scattering nanostructure for high-performance light trapping over the solar spectrum. This solar harvesting configuration consists of forward-scattering nanoparticle arrays largely embraced in an appropriate medium and partially embedded in a silicon thin film. Nanoparticles or nanoparticle clusters processing better forward-scattering than other reported structures over a wide wavelength range were obtained by tuning their magnetic and electric responses via the change of either structural configurations or surrounding media or both. Results show that lossless titania (TiO_2) nanoparticles embraced in a glass medium scatter light in forward direction and with partial embedding greatly increase the light trapping in a silicon substrate of varying thicknesses. In particular, the nanostructure, consisting of 500 nm TiO_2 nanoparticles embedded 90 nm into a 200 nm thin film silicon cell, yields an increment of 10.3 mA/cm^2 in short-circuit current density over the bare thin film silicon cell or absorbs 3.15 times as much light as the bare one.

Thin film solar cells have emerged as a promising candidate for solar energy harvesting due to its relatively low manufacturing cost.[1] One major concern with this type of solar cells is their relatively low absorption efficiency. Nanostructures of different types have been attempted to overcome the problem with some successes, which include honeycomb textured substrates,[2] nano-photonic structures,[3] moth-eye,[4] metal nanoparticle arrays,[5] nanocylinders,[6] nanopillar,[7] nanogratings[8] and photon upconversion materials.[9] However, these types of nanostructures suffer from weakness of either not being scalable or having intrinsic dissipative (or heat) losses.[10]

Lossless dielectric nanospheres have been considered for light trapping applications recently. Grandidier *et al.* employed silica (SiO_2) nanoparticles atop a thin-film amorphous silicon solar cell, where the incident light is coupled into whispering gallery modes (WGM) and the absorption inside the solar cell is enhanced.[11] Yang *et al.* went further and studied partial embedment of SiO_2 spheres.[12] Wang *et al.* applied high refractive TiO_2 index nanoparticle arrays atop silicon film cells for the enhancement of the light absorption.[13] In all these studies, the extended nanoparticles are embraced in air and no attempt has been made to make the structure strongly forward scattering.

It is known that certain nanoparticles possess mostly forward scattering. Studies have been on nanoparticles with forward scattering over a narrow band. Application of these nanoparticles for solar extraction, however, has eluded researchers thus far. One challenging issue is perhaps that such a particle is required to possess an ability to forward scattering over a wide solar spectrum. An interesting design proposed by Babicheva *et al.* utilized a Si nanoparticle array of different sizes atop a substrate to suppress the reflection of the overall configuration by tuning a π-phase difference.[14] However, this design is considered inadequate for the solar cell application, because scattering is over a narrow band and also significant loss occurs in Si nanoparticles.

In this work, a nanoparticle-medium lossless nanostructure is designed to strongly favor forward scattering for solar absorption enhancement. To our knowledge, this appears to be the first attempt

at developing forward scattering structures for light trapping over a broadband such as solar spectrum. The proposed novel forward scattering nanostructure consists of dielectric (TiO_2) nanoparticle arrays largely embraced in a compatible (glass) medium and partially embedded in a silicon substrate. The forward scattering feature is obtained by matching the magnetic and electric multipole responses of the TiO_2 nanoparticles in relation to its surrounding medium. While the existing literature focuses on narrow-band forward scattering by mainly tuning electric-magnetic responses, we found that forward scattering over broadband is possible if the effect of surrounding medium is also considered. In fact, with Mie solution and Mie-solution-based additional theorem, structured nanoparticles and/or nanoparticle clusters can be tuned into forward scattering over broadband when the medium effect is taken into consideration. To minimize the energy loss resulting from strong local field interactions in the interstitial gap between the particle and a flat surface, the TiO_2-glass medium structure is further modified such that the TiO_2 particle is also partially embedded in the Si substrate. The appropriate partial embedding in the present design is guided by the scattering chart and by the electromagnetic response at a material interface. We note that, unlike previous reported attempts to obtain "optimal" partial embedding through brutal-force trial-and-error approach, here an "optimal" embedding is achieved with the guidance from the Smith scattering chart and interface relations. Extensive numerical simulations were carried out on the proposed nanostructure. Results show that with an optimally tuned configuration, an increment of 215% in short circuit current can be obtained compared to a bare silicon film (200 nm), which is significantly better than other structures reported in literature for solar light trapping.

Fig. 1 shows the schematic of the proposed forward scattering lossless nanostructure for solar light trapping, where TiO_2 nanoparticles embraced in glass partially embedded in a Si film. In this design, the multipoles of the lossless TiO_2 nanoparticles are fine-tuned so as to scatter light mostly in forward direction over solar spectrum rather than over a narrow band. This is done by analyzing the modal behavior of the Mie analytical solution, which is essentially a superposition of multipole expansion series of the electromagnetic fields inside and outside a sphere irradiated by a plane wave incident light.[15] The modal analysis of electric and magnetic multipoles in the solar spectrum indicates that the incident light is scattered by a sphere in the forward direction whenever the scattering spectral curve of an electric multipole overlaps with that of its magnetic counterpart. Furthermore, it is found that the scattering spectral curve is a strong function of the refractive index ratio of the particle over its surrounding medium. Extensive computations were made using the recursive computational algorithm for multiple electromagnetic scattering by a cluster of structured nanoparticles, which in essence is the addition-theorem enhanced Mie solution.[16–18] The algorithm allows us to identify a wide class of nanoparticles, particle-clusters and structured nanoparticles (such as multi-core-shell structured particles) that are capable of forward scattering, among which the simplest configuration for solar light trapping application is a TiO_2 particle embraced by a glass medium. Other possible candidates, but somewhat less performing than TiO_2, include ITO (n=2, n being the real part of the refractive index) nanoparticles in the air (n=1) medium, and silicon (n=4) nanoparticles surrounded by an ITO (n=2) medium. Detailed computations also reveal that forward scattering is achieved in a particle if its refractive index is about two times that of the medium.

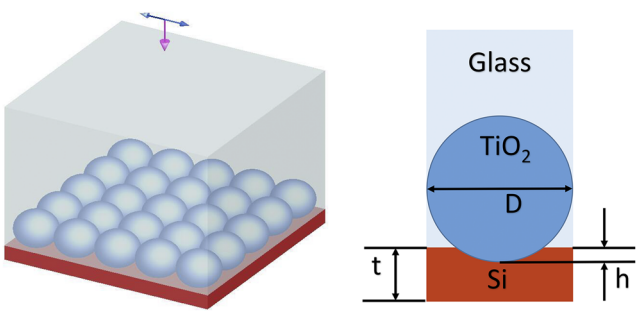

FIG. 1. 3D (left) and 2D (right) schematic of the thin film silicon solar cell with the designed nanoparticles structure.

One selected data are plotted in Fig. 2 for a TiO_2 nanoparticle in the air and in glass at the wavelength of 422 nm. Comparison of Figs. 2(a) and (d) reveals that a TiO_2 nanoparticle in glass scatters the light fully in the forward direction. For the case that TiO_2 nanoparticles in the air, the light is mainly scattered along the forward direction. However, there exists about a quarter of the energy reflected along the backward direction. Modal analysis of Mie solution for those two cases shows that the case of TiO_2 nanoparticle in glass medium satisfies the forward scattering condition. Specifically, the magnitudes of different modes, i.e., the electric and magnetic dipoles, quadrupoles, etc., are relatively the same. Also, the phase angles are about the same direction, thereby allowing forward scattering. The corresponding electric fields in the H-k plane inside the TiO_2 nanoparticle are compared in Figs. 2(b) and (e). In Fig. 2(b), the three bottom lobes along the forward direction correspond to a large forward scattering portion in the scattering pattern chart, while the top dot related to the backward portion. For the TiO_2 nanoparticle embraced in the glass medium, the electric field is concentrated at the bottom [see Fig. 2(e)]. To investigate the interparticle influence, the electric field distribution for closely packed monolayer nanoparticles in air and in glass are plotted in Figs. 2(c) and (f). It can be seen that the electric fields are squeezed towards the center and additional modes appear but the forward scattering feature remains.

Furthermore, it is found that the higher the refractive index of the nanoparticles, the larger scattering intensity is along the forward direction. For example, the peak forward scattering intensity of a TiO_2 nanoparticle reaches 80 while it is only about 40 for an ITO nanoparticle. The intensity for a silicon nanoparticle exceeds 130 because of the high real part of the index. However, the non-zero imaginary part of the index results in an irreversible energy loss and thus works against its use for solar light trapping enhancement. Moreover, by Snell's law and the relations governing the electromagnetic waves at a material interface, the reflection between a nanoparticle and the silicon substrate is minimized if the refractive index of the nanoparticles is close to that of the substrate. In light of these considerations, the configuration where a TiO_2 nanoparticle is immersed in a glass surrounding medium appears to possess the highest forward scattering intensity without any energy loss and is thus chosen for the design of the nanostructure for light trapping over the solar spectrum.

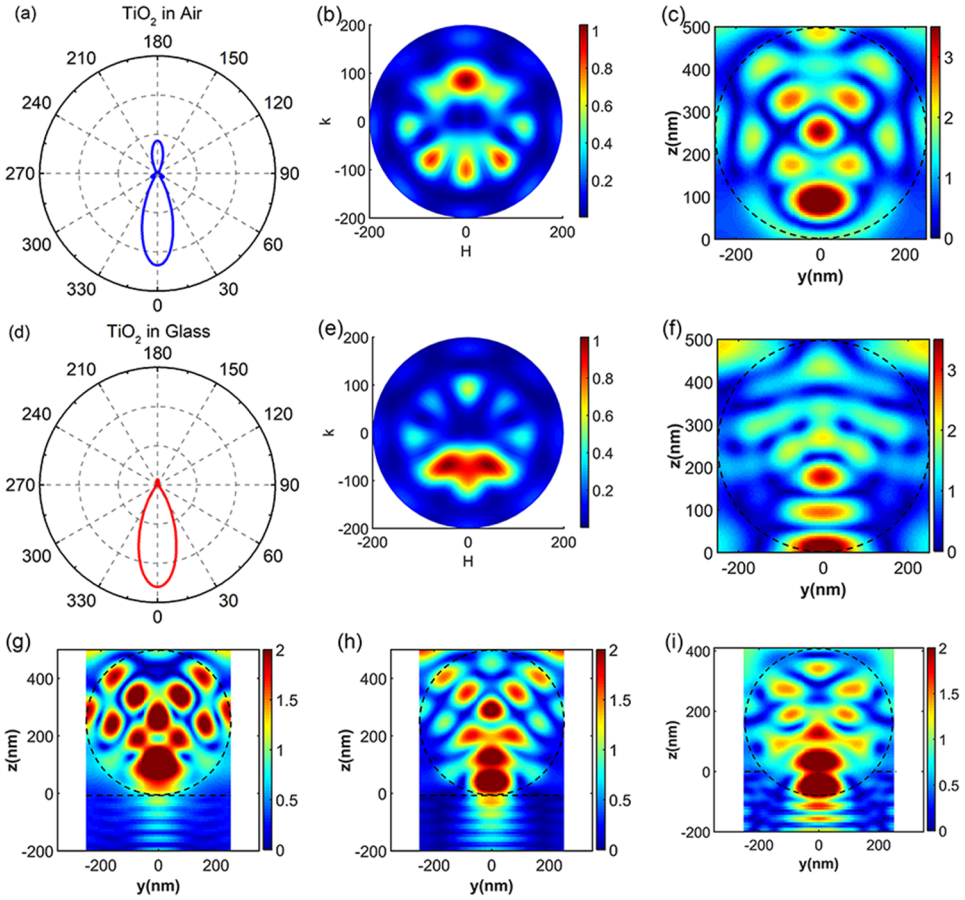

FIG. 2. The far-field scattering patterns for TiO_2 nanoparticle in (a) air and (d) glass with diameter D=500 nm at λ= 422nm. The electric field intensity calculated analytically in the H-k plane for a TiO_2 nanoparticle (b) in air and (e) in glass. The corresponding electric field intensity for TiO_2 nanoparticles arrays (c) in air and (f) in glass by FDTD simulation. The light is assumed to incident from top. The electric field distribution in the H-k plane for (g) TiO_2 nanoparticles atop the silicon film, (h) TiO_2 nanoparticles atop the silicon film with glass medium and (i) TiO_2 nanoparticles embedded 90nm inside silicon film with glass medium at λ = 422 nm.

The light trapping performance of the structure shown in Fig. 1 over a wavelength range of 300 to 1100 nm was studied using A Finite-Difference Time-Domain (FDTD) computational model based on the software LUMERICAL. To evaluate the overall optical performance, the short-circuit current density J_{sc}[13] is obtained. The integral absorption A_{int},[4] the ultimate efficiency η,[13] and the ultimate efficiency enhancement factor G[13] are also utilized to estimate the solar cell performance. Numerical accuracy is checked against analytical solutions for simple geometry before numerical details such as grid sizes and time steps were chosen for calculations.

In order to uncover the complex mechanisms behind the light enhancement of the proposed nanostructure, the performance of the Si film with various configurations, i.e., TiO_2 nanoparticles atop (Case 2), TiO_2 nanoparticles atop Si film with glass medium (Case 3) and the proposed partially embedded TiO_2 nanoparticles with glass medium (Case 4), are examined (See Fig. 3 for details). As a reference, the absorption spectrum for a bare silicon film 200 nm thick is given as case 1 in the figure.

Comparison of the TiO_2 nanoparticle atop (Case 2) and the bare Si film (Case 1) configurations indicates that the TiO_2 nanoparticle arrays atop the substrate are capable of light trapping over the entire wavelength range and provide a significant improvement to light absorption in the silicon film. However, an examination of the mode coefficients in Mie solution further reveals that for

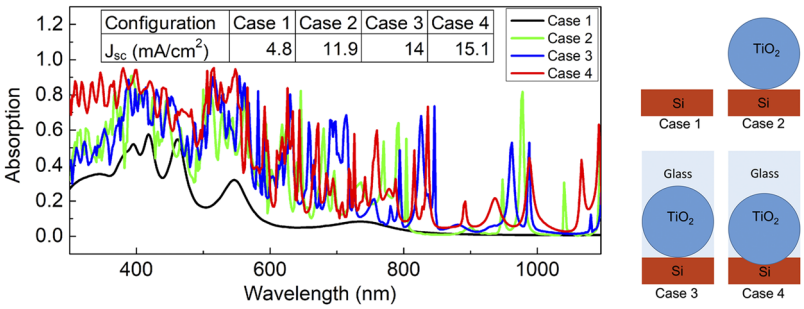

FIG. 3. The light absorption and short-circuit current density inside the Si film for each simulated configuration: (Case 1) bare silicon film, (Case 2) TiO_2 nanoparticles atop the silicon film, (Case 3) TiO_2 nanoparticles atop the silicon film with glass medium and (Case 4) TiO_2 nanoparticles embedded 90nm inside silicon film with glass medium.

the case with high refractive index nanoparticles such as TiO_2 in the air, the scattering peaks of different electric and magnetic modes are relatively separated in spectra. This means that, because of the symmetry of each mode, only a portion of the scattered light is in the forward direction and guided into the silicon thin film, while the other portion is in the backward direction and is reflected or wasted. Another shortcoming of this configuration is that there exists only a point contact between the Si substrate and a TiO_2 particle atop. As a result, considerable light energy is localized in the interstitial gap near the contact point between the surface of the substrate and the sphere. Though a portion of this energy is absorbed by the Si film, other is reflected [see also Fig. 2(g)]. Further analysis of the data shows that the short-circuit current density for Case 3 is increased by about 18% relative to Case 2 and is 2.9 times as the silicon thin film without any light trapping enhancement arrangement (Case 1).

To further reduce the energy in the interstitial gap near the contact point between the sphere and the surface, the TiO_2 nanoparticles are embedded partially into the thin film substrate (Case 4 in Fig. 3). Partial embedding of particles into a substrate to improve light trapping was studied in other configurations,[19] where random search through extensive FDTD simulations was made to determine an appropriate depth into the Si substrate. The main difference in the present study is that an optimal depth embedded into the substrate is guided by the forward scattering chart shown in Fig. 2. By the scattering pattern, the light scattered by TiO_2 in the glass is in a cone of approximately 40° in the forward direction. This translates approximately into an embedding depth/diameter being around h/D = 20%. FDTD calculations were performed for cases with varying ratios of h/D and results indicate that an optimal depth h/D = 0.18 or h = 90 nm for a D=500 nm TiO_2 in the glass.

The spectral curve of light absorption is also plotted in Fig. 3 for the configuration where TiO_2 nanoparticle arrays are embraced in glass and embedded partially into the substrate. The curve is colored red (or Case 4). By doing so, the short-circuit current density is further improved by ~10% over non-embedding. Overall, Case 4 represents an optimal nanostructured configuration for light trapping over the solar spectrum, which takes into account both forward scattering and maximum scattering contact. The light absorption enhancement mechanism can be further explained by checking the electric field distribution for the configurations, i.e., Case 2, Case 3 and Case 4, as shown in Figs. 2(g)–(i), respectively. Apparently, more light is scattered forwardly into the silicon film in the proposed nanostructure, which is in accordance with the scattering behavior. The electric field distributions, favored for light trapping, shown in Fig. 2(i), are attributed to two reasons. First, compared to the point contact between the nanoparticles and the silicon film in case 2 and 3, the partial embedment in case 4 creates more contact surface, which enables more light to leak into the solar cell. Second, it is observed that strong reflection at the gap between the nanoparticles and the silicon substrate for the case of TiO_2 nanoparticles atop. The reflection is reduced in case 4 where more contact surface exists so that the light passes directly from the nanoparticles into the Si film without passing through the nanoparticle – glass medium – Si film gap. It is worth noting that though only one wavelength is shown here, similar behavior is observed for other frequencies of relevance to solar absorption.

Figure 3 also shows that the relative absorption enhancement at wavelength below 400nm in case 4 (compared with case 2 and 3) is higher than that above 400nm. This is possible in that at a shorter wavelength, higher order modes possess more lobes in the scattering pattern along the forward direction, while only one lobe exists at a longer wavelength. In reference to Fig. 2, for nanoparticles placed atop the substrate (case 2 and case 3), a portion of the scattered light is trapped within the air gap between the nanoparticle and the Si film. By embedding the nanoparticles at an appropriate depth, this portion of the light essentially is guided directly into the Si film without passing through the gap.

FDTD simulations were also conducted to determine the effect of various parameters on the light trapping performance of the proposed nanostructure, which include the diameter of each nanoparticle D, the embedding depth h and the thickness of silicon thin film t. Fig. 4(a) plots the integral light absorption efficiency A_{int} of a 500 nm thick Si film with different combination of nanoparticle diameters and embedding depths. It is apparent that there exists an optimized ratio between the embedding depth and the nanoparticle diameter, which is about 0.2 for each case. That is, for TiO_2 nanoparticles with different diameters, i.e., 300 nm, 500 nm and 1000 nm, the optimized embedding depth are 60nm, 90nm and 200nm, respectively. This can be explained that more light is guided into the active layer as long as the embedding depth increases. However, beyond a certain point, the nanoparticles start to lose the capability of further increase in scattering, leading to a reduction of the absorption in the silicon layer.

With an optimal embedding ratio, the Si film thickness and the diameter of TiO_2 nanoparticle can be optimized. Fig. 4(b) plots the ultimate efficiency enhancement G of Si film with different diameters of the TiO_2 nanoparticle as a function of the Si film thickness t. The optimized ratio (h/D=20%) is applied for each case. The ultimate efficiency enhancement G decreases as the Si film thickness increases for each case. This is attributed to the fact that the light absorption is enhanced mostly near the nanoparticle-Si film interface. As the light further propagates into the Si film, less enhancement effect is observed. It is noted that forward scattering usually occurs over a narrow cone. For a thin film, a wide-angle scattering is more beneficial. With partial embedding and closely packed array arrangement, the forward scattering structure discussed in the present study appears to allow sufficient lateral scattering to be achieved.

In passing, we note that nanomanufacturing procedures for creating partial embedding of nanoparticles into thin films now have

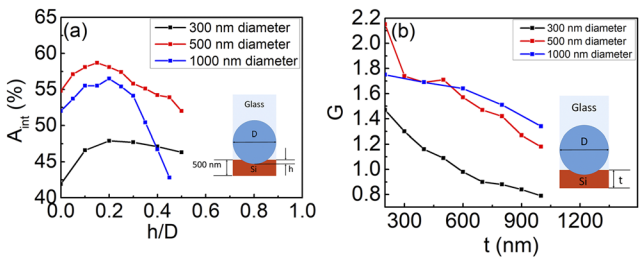

FIG. 4. (a) A_{int} of the Si thin film with different nanoparticle diameters as a function of the ratio between embedding depth h and nanoparticle diameter D. The integral absorption for the flat Si film is 23.68%. (b) G of Si film with different diameters of the nanoparticle as a function of the Si film thickness t. h/D = 20% for each case.

been well established and can be readily adopted into the existing the silicon solar cell fabrication operations.[19] One possible procedure to fabricate the designed structure can be summarized as follows. Firstly, clean a glass substrate and spin coating a layer of photoresist on it. Secondly, transfer a monolayer of TiO_2 nanoparticles on top of the photoresist coating. Then, deposit a Si film to cover the nanoparticles, which followed by removing the photoresist with acetone. Selectively ion etch the Si film with SF6 plasma to expose the TiO_2 nanoparticles, which forms the partial embedding nanoparticles-Si film structure. Finally, deposit a SiO_2 layer to on top of the whole structure.

In summary, this paper has presented a novel nanostructure, consisting of TiO_2 nanoparticle arrays embraced in a glass medium and partially embedded a thin film Si solar cell, for light trapping over the solar spectrum. An addition-theorem recursive electromagnetic computational algorithm has been applied to identify forward-scattering nanoparticle structures by matching the multi-mode magnetic and electric responses through tuning the structural parameters of nanoparticles or particle clusters in relation to their surrounding media. The TiO_2 nanoparticles in glass medium is considered as an optimal choice. Light reflection is further reduced by embedding the nanoparticles partially into the substrate. The effect of the Si film thickness, the nanoparticle diameter, and the embedding depth was studied. An short-circuit current density enhancement of 215% over a bare thin film Si cell (or 3.15 times light absorbing) can be achieved with a nanostructure of 500nm TiO_2 nanoparticles with a 90nm embedding depth in a 200nm thick thin film silicon cell. In practical application, the design methodology is also applicable for solar cells with different thicknesses and different types, i.e., GaAs solar cell, organic photovoltaics and perovskite solar cell.

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