

# Scattering of light into silicon by spherical and hemispherical silver nanoparticles

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The interaction of light with noble metal nanoparticles deposited onto the top surface of a semiconductor has been investigated using the finite-difference time-domain method. The scattering is calculated for spherical and hemispherical silver nanoparticles placed in a periodic two-dimensional array on the upper surface of a semi-infinite silicon substrate. The results show that the contact area between hemispherical particles and the silicon significantly reduces the forward scattering. The use of an oxide buffer layer to separate the particle from the semiconductor is investigated and is seen to be important if the forward scattering of light is to be enhanced. © 2009 Optical Society of America  
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There has recently been considerable interest in enhancing the performance of silicon solar cells using noble metal nanoparticles [1–8]. Catchpole and Polman [3] used finite-difference time-domain (FDTD) simulations to model the scattering of light by silver nanoparticles separated from the substrate by a 10-nm-thick SiO<sub>2</sub> layer. They reported that the forward scattering of light into the substrate increased with contact area between the nanoparticle and the oxide layer. Calculations by Häggglund *et al.* [4], however, suggest that if the upper and lower parts of a nanoparticle oscillate out of phase, forward scattering is reduced. This scenario would occur if a hemispherical particle is in direct contact with a dielectric since the upper and lower internal fields are different. These works appear to be contradictory and therefore we have investigated the scattering of light, when silver nanoparticles are placed on the top surface of a silicon substrate or SiO<sub>2</sub> layer, using the FDTD technique [9]. Indeed the effect of an oxide layer has been highlighted by Temple *et al.* [7] as an area requiring attention.

Increasing the forward scattering into the silicon is considered the important mechanism for enhancing the performance of inorganic solar cells [4,7], although near-field enhancements may be important if very thin films are being considered [8]. Here we consider particles in tightly packed arrays, an area yet to receive much attention in previous studies.

In our calculations the nanoparticles are in periodic arrays on the upper surface of a silicon substrate or on a thin SiO<sub>2</sub> layer. The dielectric function of silver is represented using a Drude model,

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (1)$$

where  $\omega_p$  is the bulk plasmon frequency and  $\gamma$  is the characteristic collision frequency. In our calculations  $\varepsilon_{\infty} = 5.7$ ,  $\omega_p = 1.3673 \times 10^{16}$  rad/s, and  $\gamma = 2.7335 \times 10^{15}$  Hz.

At wavelengths in the proximity of the surface plasmon resonance noble metal nanoparticles have a negative dielectric constant. This enables the particle to interact with light over a cross-sectional area greater than its geometrical cross-sectional area [8]. The absorption and scattering cross-sectional areas,  $C_{\text{abs}}$  and  $C_{\text{sca}}$ , are given by [10]

$$C_{\text{abs}} = \frac{2\pi}{\lambda} \text{Im}[\alpha], \quad (2)$$

$$C_{\text{sca}} = \frac{1}{6\pi} \left( \frac{2\pi}{\lambda} \right)^4 |\alpha|^2, \quad (3)$$

where  $\lambda$  is the wavelength and  $\alpha$  is the polarizability of the particle,

$$\alpha = 3V \frac{\varepsilon - 1}{\varepsilon + 2}, \quad (4)$$

with  $V$  being the volume of the sphere and  $\varepsilon$  being the dielectric function, given by Eq. (1).

Figure 1 shows the ratio  $C_{\text{sca}}/C_{\text{abs}}$  for a 60 nm diameter silver sphere. The wavelengths where the ratio is much greater than 1 are where the enhance-

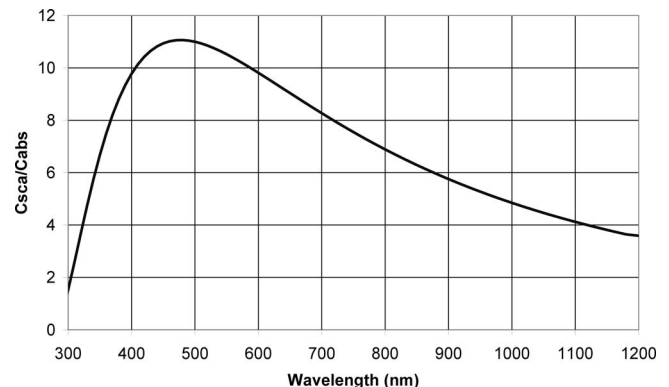


Fig. 1. Ratio of scattering to absorption cross-sectional area ( $C_{\text{sca}}/C_{\text{abs}}$ ) for a 60 nm diameter silver sphere.

ment of the forward scattering into the semiconductor is likely to occur. At wavelengths where  $C_{\text{abs}} > C_{\text{sca}}$  there is a significant amount of absorbed light that will not contribute to the photovoltaic conversion.

The scattering is found by considering power flow across two computation surfaces extending the full length and width of the FDTD workspace as depicted in Fig. 2. Reflections from the semiconductor's back surface are minimized by extending the silicon into a perfectly matched layer (PML), making it appear to be semi-infinite. This is necessary because any reflections will travel through the lower computational surface and cannot be separated from the forward scattered waves. A number of models were run to find appropriate distances of these surfaces from the silver particles. For the largest spherical particles it was found that the solutions converged when the surfaces were more than 70 nm from the spheres. For hemispherical particles placed on the silicon, this distance had to be increased to at least 100 nm. In all our calculations the computational surfaces were 150 nm from the silver particles.

The top of the computational domain was also terminated by a PML, with the other four FDTD workspace boundaries being periodic. The periodic boundaries ensured that all scattered fields pass through one of the computational surfaces. The incident field was a Gaussian pulse of  $y$ -polarized electric field.

The discretization of the computational domain into FDTD cells must be fine enough to ensure a convergent solution. An extensive numerical experimentation was carried out by increasing the number of cells until the convergence was obtained. The dimensions of the FDTD cells for the results reported here are between 1 and 2 nm.

Absorption in our calculations was due to losses in the silver. It should be noted that for predicting photovoltaic conversions in real devices absorption in the silicon should be included, but in this work we were primarily interested only in finding the increased forward scattering at wavelengths beyond 450 nm. For wavelengths longer than 450 nm the extinction coefficient of the silicon is below 0.1 and the refractive index of the material is less than 4.7 [11]. A very simple model was therefore used to represent the silicon as a

material with a real refractive index of 3.5 ( $\epsilon_r = 12.25$ ). The advantage of this simple material model is that the placement of the computational surface for predicting forward scattering depends only on being far enough away from the nanoparticle to be unaffected by the strongly localized near field.

Absorption, backscattering, and near-field coupling between the nanoparticles are considered loss mechanisms, as they would not contribute to improved photocurrent response in a solar cell. All the calculations were carried out for infinite two-dimensional arrays of particles by making the distance between the periodic boundaries, in the  $x$  and  $y$  directions, equal to the center-to-center separation distance of the particles.

The results of forward scattering for separation distances of 100 and 75 nm are shown in Fig. 3. The forward scattering is normalized to that obtained when no nanoparticles are present on the silicon surface. It is seen that larger-diameter spheres cause an increased forward scattering at longer wavelengths. This is consistent with results reported previously (see, for example, [1–7]). There is reduced forward scattering at the shorter wavelengths due to both increased absorption and backscattering by the silver nanoparticles. The shortest wavelength at which the enhancement occurs depends on the separation distance as well as on the particle size.

To consider the effect of the contact area between the nanoparticles and silicon the scattering due to 60 nm diameter hemispheres with a center-to-center separation of 75 nm and the flat surface placed on the semiconductor was calculated (Fig. 4). The forward scattering for 60 nm spheres with the same separation is included in Fig. 4 to enable comparison. It can be seen that the hemisphere causes significantly more backscattering and reduced forward scattering. In fact, forward scattering into the silicon with no particles present would be 0.7 and so, except for a very narrow band, the hemisphere actually reduces the forward scattering. This result shows that a spherical particle shape is the most desirable for enhancing forward scattering, as previously suggested by Hägglund *et al.* [4], owing to the minimal contact

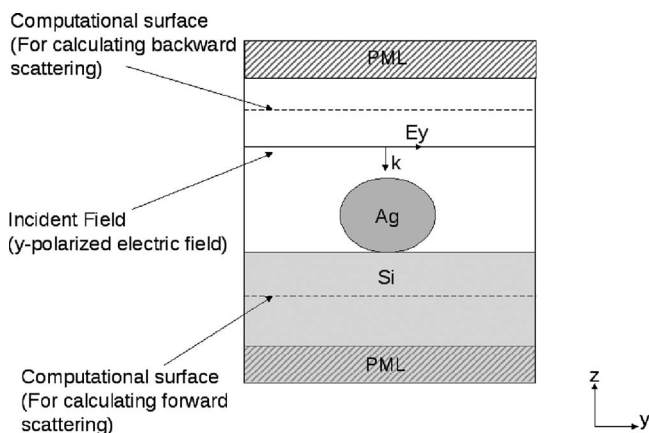


Fig. 2. Cross section at  $x=0$  of the FDTD computational domain.

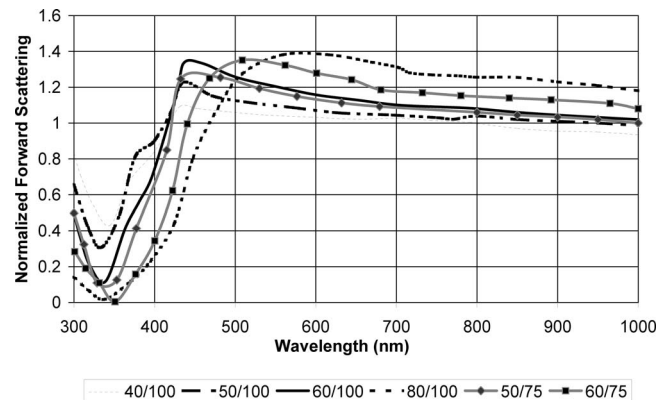


Fig. 3. Normalized forward scattering for spherical particles in a two-dimensional periodic array. In the legend the number before the slash is the diameter of the sphere, and the other number represents the center-to-center spacing between particles.

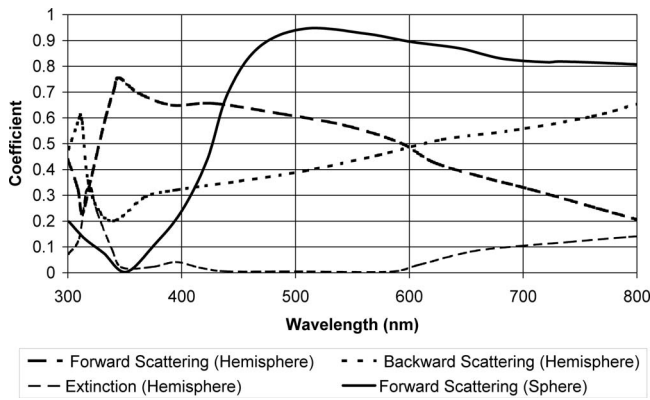


Fig. 4. Forward scattering, backward scattering, and extinction coefficients for a 60 nm diameter hemispherical particle on the top surface of semi-infinite silicon. Forward scattering due to a 60 nm sphere on silicon is included for comparison. Scattering is not normalized in this figure.

area between the nanoparticle and the silicon. Unfortunately the preferred production method of annealing Ag layers to produce nanoparticles [1,7] typically produces hemispherical particles.

Calculations by Hägglund *et al.* [4] involving a gold disk indicated that the effects of the dielectric substrate on the nanoparticle are reduced if it is lifted off the surface. Figure 5 shows the results for 60 nm diameter hemispheres separated from the silicon by  $\text{SiO}_2$  layers of various thicknesses. The  $\text{SiO}_2$  was in-

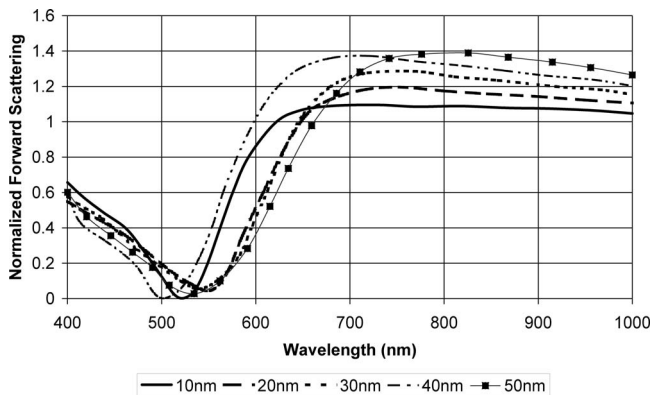


Fig. 5. Normalized forward scattering when 60 nm spherical hemispheres are separated from the silicon using  $\text{SiO}_2$  films. The legend indicates the thickness of the  $\text{SiO}_2$  film.

cluded in the FDTD model using a dielectric constant for the material of 2.8, derived from the data presented by Dionne *et al.* [12]. It can be seen that for all the thicknesses of  $\text{SiO}_2$  considered enhancement of the forward scattering occurred for wavelengths above 680 nm. This compares with the enhancement starting at 438 nm for the 60 nm spherical particles on the silicon. The magnitude of forward scattering above 700 nm is seen to be dependent on the thickness of the oxide layer.

In this work we demonstrated that the contact area between the particles and the semiconductor causes a reduced forward scattering but an oxide layer can be used to counteract this reduction. All the calculations reported here consider the case of closely packed arrays rather than isolated particles. It is shown that the separation between particles modifies the maximum forward scattering enhancement and the wavelength at which it begins.

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