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Enhanced light trapping using plasmonic nanoparticles

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Abstract. Plasmonics is a new light trapping method used in photovoltaic (PV) solar cells. A significant enhancement of the scattered and absorbed incident light due to the use of silver nanoparticles (Ag-NPs) was observed, which yield to the exaltation of the electromagnetic field in the vicinity of these NPs. In this context, we investigate optically and morphologically the effect of the NPs size dependence on the localized surface plasmon resonance. Extinction, absorption and scattering cross sections are calculated using Mie theory.

1. Introduction

Plasmonic field has recently attracted attention in silicon-based photovoltaic devices due to its exceptional properties [1-4]. Interacting with sun light, metal NPs can support localized surface plasmon resonance (LSPR) caused by the collective oscillations of their conduction electrons. The excitation of surface plasmon leads to an extraordinary scattering [5] and a strong enhancement of local field in the vicinity of the NPs surface [6, 7]. This enhancement increases the optical path of light inside the active layer [8]. This considerably contributes to the increase of the photo-generated current as more light is absorbed and collected. Noble metals like gold (Au) and silver (Ag) are best candidates to support localized surface plasmon, where light can resonantly be scattered or absorbed in accordance with NPs size, shape, inter-distance and surrounding medium [9-11]. Silver would be a better choice than gold because it has the higher scattering efficiency as well as the lower wavelength interband transition [12, 13].

Modeling the optical response of Ag-NPs interacting with sun light can be based on Mie theory [14]. NPs are supposed to be spherical (radius \( R \)) in a non absorbing medium (air with a refractive index \( n_a \)). Within this theory, the extinction \( \sigma_{\text{ext}} \), scattering \( \sigma_{\text{sca}} \) and absorption \( \sigma_{\text{abs}} \) cross sections are expressed in series expansion of the involved fields [15], which are described in terms of spherical harmonic functions, such that, the different multi-polar excitations and their contribution can be easily identified:

\[
\sigma_{\text{ext}} = \frac{2\pi}{k^2} \sum_{j=1}^{\infty} (2j+1) \text{Re}(a_j + b_j)
\]
\[ \sigma_{\text{sca}} = \frac{2\pi}{k^2} \sum_{j=1}^{\infty} (2j+1) \left[ |a_j|^2 + |b_j|^2 \right] \]  
\[ \sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{sca}} \]  

Where \( k = (2\pi N)/\lambda \), \( \lambda \) is the wavelength of the incident light, \( N \) is the refractive index of the medium surrounding the particle, \( a_j \) and \( b_j \) are defined as follows:

\[ a_j = \frac{m \psi_j(w) \psi_j'(v) - \psi_j(v) \psi_j'(w)}{m \psi_j(w) \xi_j(v) - \xi_j(v) \psi_j'(w)} \]  
\[ b_j = \frac{\psi_j(w) \psi_j'(v) - m \psi_j(v) \psi_j'(w)}{\psi_j(w) \xi_j(v) - m \xi_j(v) \psi_j'(w)} \]  

In these expressions, \( \psi_j \) and \( \xi_j \) are Ricatti-Bessel functions and dimensionless parameters are defined as:

\[ m = N / n_m \]  
\[ \nu = k / R \]  
\[ w = kc / n_m \]  

In this work, we investigate in a first part the effect of NPs size on the enhancement of scattered or absorbed light. Then we study experimentally the effect of mass thickness on the optical and morphological properties of Ag-Nps.

2. Experimental details
Silver (Ag) thin films were deposited on silicon substrates (p-type, (100) oriented, 300 μm-thick) by thermal evaporation technique. In order to eliminate organic and inorganic impurities from the surface, silicon wafer was ultra-sonicated sequentially in deionized water, acetone and ethanol for 15 mn at 40 °C. Ag with mass thicknesses of nearly 5, 10, 15 and 20 nm was then evaporated at chamber pressure of 10^{-6} mbar while maintaining a low deposition rate (0.1 Å/s) in order to cover homogenously the silicon surface. To break continuous film into agglomerates, samples were annealed under argon atmosphere during 60 min at 250°C. In order to investigate the effect of NPs size on the light scattering, absorption, scattering and extinction cross sections of various radiiuses are calculated using Mie Theory (matlab code). Total reflectance was measured using a Perkin Elmer Lambda 950 UV-Vis-NIR (250 – 2500 nm) spectrophotometer equipped with an integrating sphere. JEOL FEG Scanning Electron Microscope (SEM) was used to study the morphology of Ag-NPs. Images taken from SEM are analyzed quantitatively and qualitatively using an image processing and analysis software (Image J, Ref [16]). Our study investigates the effect of particles size, film thickness and coverage rate on the optical properties including extinction, reflection and LSPR peaks shift related to metal Nps.

3. Results and discussions
Focusing on the change in the NPs size, LSPR peaks shift was theoretically investigated using Mie theory [17]. Incident light interact effectively with Ag-NPs for cross sections larger than the geometrical cross section [18]. In fact, the size of the NPs has a considerable effect on LSPR and consequently on their optical properties. Two different mechanisms can be distinguished inducing size dependence of the LSPR properties. Below 50 nm of radius, light tends to be absorbed than scattered [19]. For this size range, we may assume that NPs are properly described by a dielectric dipole. Size
dependence of the LSPR mainly affects the intensity of the resonance band while the effect on the resonance wavelength is quite reduced leading to a small shift towards lower frequencies (figure 1a).

![Figure 1](image_url)

**Figure 1.** Calculated extinction, absorption and scattering cross sections of Ag-NPs in vacuum (air) with 20 nm (a) and 60 nm (b) radius. Measured values for the dielectric function $\varepsilon(\omega)$ are taken from Johnson and Christy database [18].

Up to 50 nm, light wavelength is quite larger than NPs size. Therefore, NPs are not well described by a dipole and then multi-polar terms are required. For larger particle sizes, the excitation of higher-order plasmon modes must be taken into consideration. The spectral response is modified due to both retardation effects and appearance of high order mode in the Mie scattering coefficients (figure 1b). The resonance band splits into several bands: one band for dipolar, two bands for quadrupolar, three bands for octopole, etc. In this case, scattering pre-dominates absorption since retardation effects become more and more important. Figure 2 depicts the normalized extinction cross section for different radius of Ag-NPs. We can clearly observe the red-shift and broadening of the resonance band with the increase of the particle size. This makes the Ag-NPs a very efficient tool for solar cells as we can manipulate light trapping and scatter most of the radiation with the largest angular spread in order to maximize the optical path length.

![Figure 2](image_url)

**Figure 2.** Calculated extinction cross section of Ag-NPs in vacuum (air) with 20, 40, 60, 80 and 100 nm radius.
According to Mie theory calculation of absorption and scattering cross section, it is clear that the spectral resonance position and strength of the dipole as well as of the high-order mode depend noticeably on the dimension of the NPs. To correlate with experiment, a morphological study is necessary. For this purpose, we deposited Ag thin films of nearly 5, 10, 15 and 20 nm thicknesses on silicon substrate. Annealing steps under a neutral atmosphere (argon) is necessary to break continuous films into agglomerated islands. Annealing was carried out at 250°C during 60 min. Shape, size and surface coverage rate of Ag-NPs depend on the thickness of the deposited films and annealing parameters (time and temperature). Table 1 shows morphological characteristics derived from SEM images and analyzed by Image J software.

<table>
<thead>
<tr>
<th>Mass thickness (nm)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface coverage rate (%)</td>
<td>4</td>
<td>9</td>
<td>57</td>
<td>74</td>
</tr>
<tr>
<td>Average particles size (nm)</td>
<td>18</td>
<td>25</td>
<td>60</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 3 shows SEM images (a, b, c and d) and size distribution (e,f,g and h) of Ag-Nps. By increasing the mass thickness, and then the NPs size, the surface coverage rate significantly increases from 4 % to 74 %. Furthermore, Ag-NPs become more interconnected, elongated and larger in size. The average particles size increases from 18 nm to 80 nm for 5 and 20 nm mass thickness respectively. It is obvious from figure 3d (20 nm mass thickness) that the annealing parameters are not sufficient enough to compress the NPs and to transform elongated NPs to regular spheroids.

The optical response of Ag-NPs depends essentially on size, shape and surface coverage rate. Figure 4 shows the total reflectance for Ag-NPs layers deposited on silicon substrate with various mass thicknesses. For 5 nm thickness, the resonance modes are lost due to the weak coverage rate. NPs are slightly distributed on the surface of silicon, as can be seen in figure 3a. The reflectance spectrum corresponding to 5 nm mass thickness has almost the same aspect than that of the silicon substrate. While for 10 nm mass thickness, which corresponds to NPs size of about 25 nm, the first peak located at 365 nm appears. According to Mie theory, this can confirm the dependence of the resonance mode on NPs size for dimensions below 50 nm. For the two other samples (15 nm and 20 nm mass thickness), two resonance peaks appear due to the excitation of the high order mode. The shorter wavelength peaks maximum corresponds to quadrupolar resonance whereas longer wavelength maximum peak corresponds to dipolar resonance. The peak of dipolar related band is red-shifted and broadened from 500 nm to 580 nm as the mass thickness increase from 15 nm to 20 nm. The red-shift leads to an increase of the reflectance intensity of the maximum of the dipolar peak, which in turn is due to the retardation effects of the electromagnetic field across the nanoparticles as their size increases [21].
Figure 3. SEM images of Ag-NPs with mass thicknesses corresponding to (a) 5 nm, (b) 10 nm, (c) 15 nm and (d) 20 nm grown on silicon substrates and annealed at 250° C during 60 min. (e), (f), (g) and (h) correspond to the NPs size distribution, respectively.
4. Conclusion
The resonant nature of plasmonic enhancement of the Ag-NPs is investigated in this work. We theoretically demonstrate that the absorbed part of light by small NPs is much higher than the scattered part, while scattering is much important for larger NPs due to the excitation of high order modes. With the increase of mass thickness of silver thin films deposited by thermal evaporation and depending on the size of annealed Ag-NPs, experimental reflectance spectra are proven to be mainly affected.

5. References
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