The effect of plasmonic particles on solar absorption in vertically aligned silicon nanowire arrays

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(Received 2 July 2010; accepted 14 July 2010; published online 17 August 2010)

In this paper, we used the finite-difference time domain method to determine whether metallic caps provide plasmonic enhancement of absorption in vertically aligned silicon nanowire arrays. Metallic caps result naturally from the vapor-liquid-solid growth process, which uses metal catalyst particles to initiate growth. We found that gold, copper, and silver catalysts all decrease the integrated optical absorption across the solar spectrum. *© 2010 American Institute of Physics.*
[doi:10.1063/1.3475484]

Solar cells based on radial *p-n* junction silicon nanowire (SiNW) arrays have been proposed as candidates for next-generation photovoltaics.[1,2] Vertically oriented nanowire arrays can be fabricated using a patterned vapor-liquid-solid (VLS) growth method with noble metal particle catalysts.[3,4] The limiting theoretical efficiency of such arrays is only partially understood.[5] Our previous work[6] showed that ideal vertically aligned SiNW arrays can be more absorptive than an equally-thick silicon solid film, a conclusion reached by other authors for related systems.[7] However, these works did not consider the role of metal catalyst particles. At the conclusion of growth, the metal forms a hemispherical cap on the nanowire, which can optionally be removed. While enhanced near fields near gold-capped nanowires have previously been studied for surface or tip enhanced Raman scattering,[8] the effect of metal caps on absorption has not been modeled in the photovoltaic context. Given the large body of recent work on plasmonically enhanced solar cells,[9–18] it is a fundamental question to ask whether metal caps increase the optical absorption in SiNW photovoltaic systems.

Here we carry out calculations to show that, in contrast to other photovoltaic devices, metallic particles degrade the integrated optical absorption in vertically oriented SiNW array solar cells. Our work contributes to understanding the efficiencies that can ultimately be achieved in nanowire solar cells. Measured experimental efficiencies depend on both optical and electronic transport properties. In addition to affecting absorption, metallic caps can introduce impurity states into the nanowires or change the contact resistance. One recent experiment demonstrated that a gold-capped SiNW solar cell had higher short circuit current than its counterpart with the caps removed.[19] By simulating metal-capped nanowire arrays, we isolate the effect of metallic particles on absorption to understand the role of plasmonic effects.

Using finite-difference time domain (FDTD) modeling, we study how the diameter and spacing of the nanowires and the composition of the metal caps affect the integrated absorption across the solar spectrum. We find that for a wide range of nanowire diameters and spacings, metallic caps degrade the integrated absorption in the photoactive region. This conclusion holds true even without considering additional parasitic absorption due to impurity states. We discuss why the two common mechanisms for plasmonic enhancement in thin-film photovoltaic systems, the excitation of localized particle resonances and the use of metallic particles to excite guided modes, do not increase efficiencies in the case of nanowire arrays.

Figure 1(a) illustrates the structure under study, a vertically aligned SiNW array with hemispherical metal caps. The array is illuminated from the top by sunlight (red arrow). The electric field of the incident light is polarized along the *x*-axis. The array consists of SiNWs with diameter d and period a arranged in a square lattice, as shown in Fig. 1(b). Each nanowire has a hemispherical metal cap. The diameter of the cap is equal to the diameter d of the SiNW beneath, as shown in Fig. 1(c). The shape of the metallic particle is similar to that seen in TEM pictures of VLS-grown SiNWs in the literature.[20] We fixed the length L of the SiNWs to be 500 nm. The diameter was varied between 100 and 500 nm and the lattice constant was varied between 100 and 1050 nm.

Optical constants for silicon and metal were taken from the literature.[21] We assume that the SiNWs are lightly doped, so that both *n*-type and *p*-type regions can be modeled using the same refractive index and absorption coefficient as intrinsic crystalline silicon. Gold, copper, and silver particles were studied. All three noble metals have been used for VLS growth of SiNWs.[22] We study illumination under the Ameri-

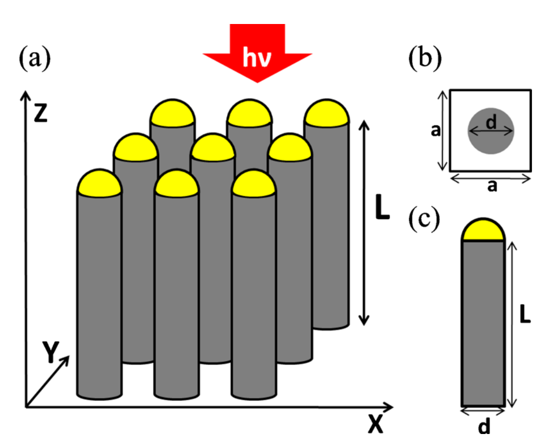

FIG. 1. (Color online) (a) Schematic of the SiNW array with hemispherical metal caps. (b) Top view of a single nanowire. (c) Cross sectional view of a single nanowire.

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can Society for Testing and Materials (ASTM) air mass 1.5 global solar spectrum. For photovoltaic applications, the wavelength range of interest is 400 to 1100 nm.

We calculate the absorption of the nanowire array using the FDTD method,[23] using the commercial LUMERICAL package. The code uses an improved model to effectively fit the experimentally measured optical constants.

We calculate the absorption within the photoactive silicon region; increased absorption corresponds to higher photocurrent and higher efficiency. We define a figure of merit equal to the photon flux absorbed in the SiNW layer normalized by the total incident photon flux as follows:

$$\text{F.O.M.} = \frac{\int_{400\ \text{nm}}^{1100\ \text{nm}} \frac{\lambda}{hc} I(\lambda) A(\lambda) d\lambda}{\int_{400\ \text{nm}}^{1100\ \text{nm}} \frac{\lambda}{hc} I(\lambda) d\lambda},$$

in which λ is the wavelength, $I(\lambda)$ is the spectral irradiance of the ASTM air mass 1.5 global spectrum, and $A(\lambda)$ is the absorptance inside the silicon calculated by FDTD. The sampling interval in the numerical integration is 1 nm.

To determine whether the metal caps increase or decrease absorption inside the SiNW layer, we study the *absorption ratio*, defined as the ratio between the F.O.M for the SiNW array with and without metal caps.

Figure 2 shows the calculated absorption ratio for gold (a), copper (b), and silver (c) caps. We observe that the absorption ratio for gold is always below 1; in other words, gold caps decrease the absorption in the nanowires. Copper caps also decrease absorption and have the lowest absorption ratio of the three metals. Bulk silver has lower loss than gold or copper in the solar spectrum. We observe that silver caps provide slightly higher absorption ratios than gold or copper. The highest absorption ratio is close to 1.

To understand why metal caps degrade the absorption ratio, we compare absorptance spectra for bare and capped nanowire arrays. Figure 3(a) shows the spectrum for a silver-capped array with $d=a=100$ nm. In this case, the nanowire diameter is equal to the lattice constant and the metal caps touch. The silver-capped array exhibits lower absorptance than the uncapped array across the entire spectrum. This case corresponds to a low overall absorption ratio [Fig. 2(c)]. Figure 3(b) shows results for a silver-capped array with $a=450$ nm and $d=100$ nm. In this case, the nanowires are well separated. The absorptance spectrum for the silver-capped array shows an enhancement peak around 840 nm. We have verified by inspection of the near-field electric field intensity that this peak is due to the excitation of a localized surface plasmon on the cap. However, the absorptance spectrum for the capped array is lower than the bare array for lower wavelengths. As a result, the absorption ratio is close to 1 [Fig. 2(c)].

The effect of plasmonic enhancement on the integrated absorption is weak for the metal-capped nanowire geometry. In Fig. 3(b), the plasmon resonance of the metal cap occurs in the red/near-IR range. Compared to a metal cap in vacuum, the resonant wavelength is redshifted due to the presence of the silicon nanowire. As the nanowire diameter increases from 100 nm, the plasmon resonance shifts to higher wavelengths at which the solar irradiance is lower. For *spherical* metal caps (not shown), we have observed that the plasmon wavelength is shorter, yielding higher absorption ratios (1.2 at maximum).

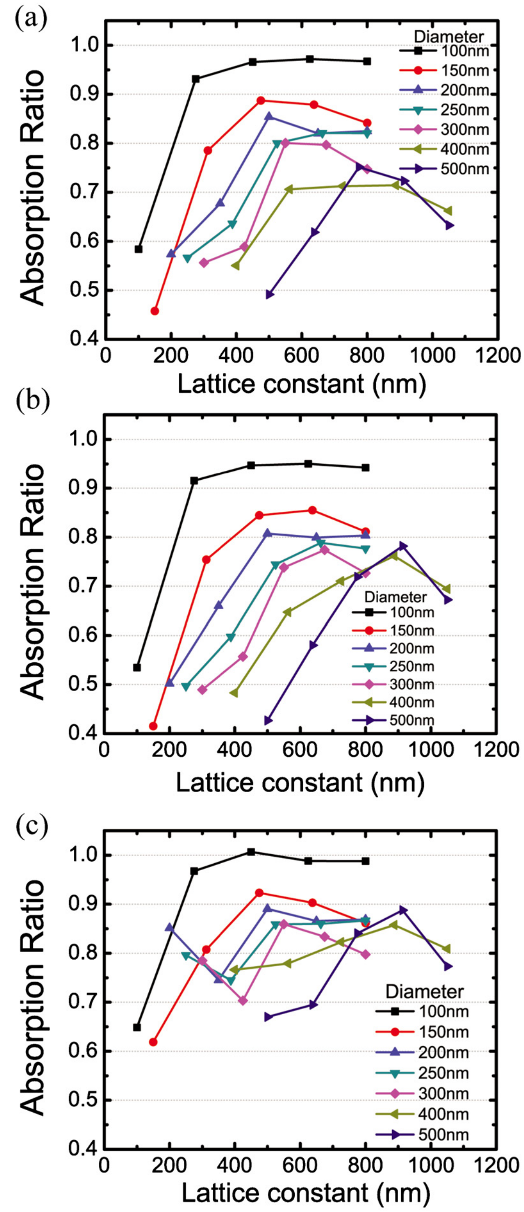

FIG. 2. (Color online) Absorption ratio for SiNW arrays with (a) gold, (b) copper, and (c) silver hemispherical metal caps.

We have calculated the absorption ratio as a function of nanowire length for a configuration with high absorption ratios, $a=500$ nm and $d=100$ nm (not shown). We observed that the absorption ratio decreases with decreasing wire length between 2 μm and 100 nm. For all lengths, silver has the highest absorption ratio and copper has the lowest; all values are less than or equal to 1.

In this paper, we have calculated the effect of gold, copper, and silver metallic caps on the absorption in silicon nanowire arrays. In most cases, we find that the metal caps decrease integrated absorption. We note that the effect of metallic impurities in the silicon, not considered here, could further degrade performance.

Our result stands in contrast to a large body of work reporting on plasmonic enhancement of optical absorption. We attribute this result to particular features of metal-capped silicon nanowire arrays.

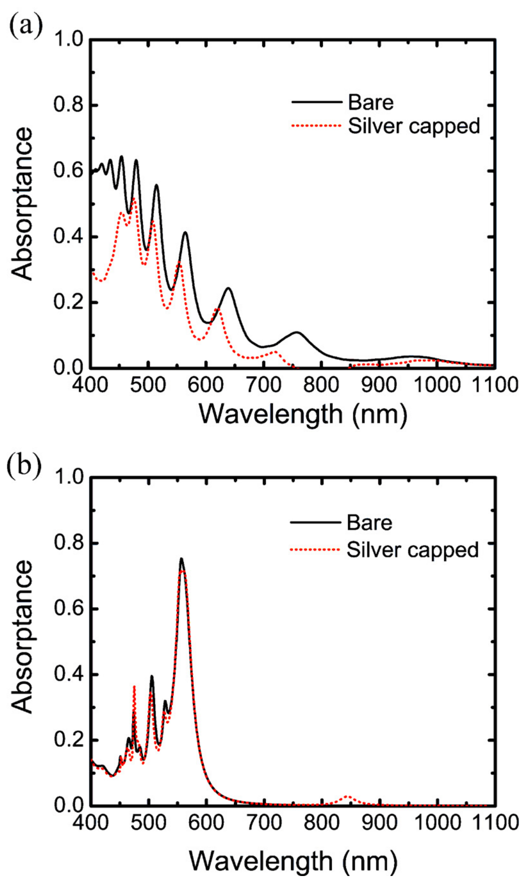

FIG. 3. (Color online) The absorptance spectrum of bare (solid) and silver capped (dotted) SiNW arrays with $L=500$ nm, $d=100$ nm, and $a=100$ nm (a) and 450 nm (b).

First, the metal caps resulting from VLS growth have a diameter equal to the nanowire diameter. Under this constraint, the localized plasmon resonance of the cap occurs in the red/near-IR range of the spectrum and does not provide enough enhancement to offset the lower absorption at short wavelengths. Overall, the integrated absorption performance is similar to or worse than a bare array. The plasmon resonance may be useful for near-IR photodetectors.

Second, while metal particles or gratings have often been used to couple light into the guided modes of a photoactive layer, enhancing absorption, such an effect is not necessary here. The silicon nanowire array itself, due to its two-dimensional periodicity, already provides this coupling, as we have shown in previous work.[6]

For silicon nanowire solar cells grown by VLS methods, the overall cell efficiency will not only depend on the optical absorption properties but also the electrical collection efficiency. Further study will be required to untangle these effects. However, our results suggest that care must be taken in applying the concept of plasmonic enhancement to solar cell designs; the "plasmonic solution" is not universally valid. The nanowire geometry studied here provides an illustrative example of how plasmonic particles can degrade optical performance.

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