

Plasmonic core-shell gold nanoparticle enhanced optical absorption in photovoltaic devices

Di Qu, Fang Liu, Jiafan Yu, Wanlu Xie, Qi Xu, Xiangdong Li, and Yidong Huang

Citation: [Applied Physics Letters](#) **98**, 113119 (2011); doi: 10.1063/1.3559225

View online: <http://dx.doi.org/10.1063/1.3559225>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/98/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

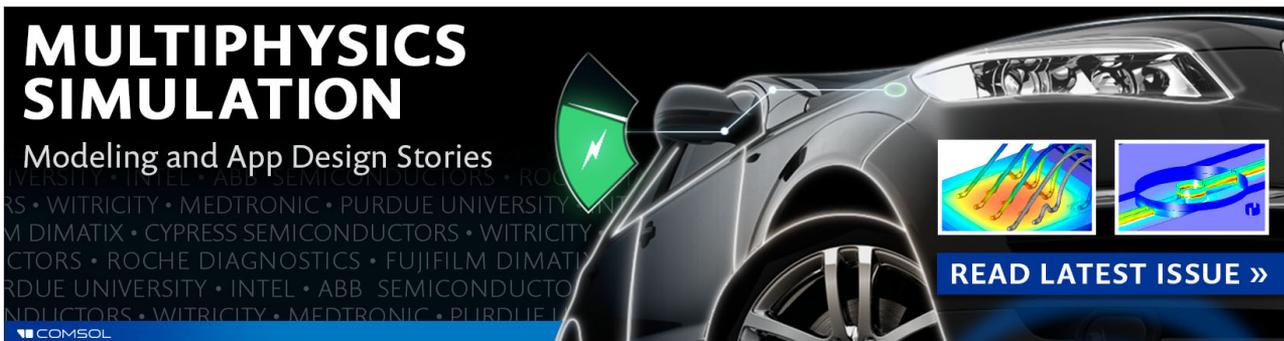
[The effect of ageing on the scattering properties of silver nanoparticles for a plasmonic solar cell](#)
J. Appl. Phys. **118**, 153102 (2015); 10.1063/1.4933378

[Enhancing the photocurrent and photoluminescence of single crystal monolayer MoS₂ with resonant plasmonic nanoshells](#)
Appl. Phys. Lett. **104**, 031112 (2014); 10.1063/1.4862745

[Plasmonic Au nanoparticles on 8 nm TiO₂ nanotubes for enhanced photocatalytic water splitting](#)
J. Renewable Sustainable Energy **5**, 053104 (2013); 10.1063/1.4821177

[Tunable infrared plasmonic absorption by metallic nanoparticles](#)
J. Appl. Phys. **110**, 046101 (2011); 10.1063/1.3624596

[Multimodal plasmon coupling in low symmetry gold nanoparticle pairs detected in surface-enhanced Raman scattering](#)
Appl. Phys. Lett. **98**, 183115 (2011); 10.1063/1.3555429



**MULTIPHYSICS
SIMULATION**

Modeling and App Design Stories

UNIVERSITY • INTEL • ABB SEMICONDUCTORS • ROCH
RS • WITRICITY • MEDTRONIC • PURDUE UNIVERSITY • IN
M DIMATIX • CYPRESS SEMICONDUCTORS • WITRICITY
CTORS • ROCHE DIAGNOSTICS • FUJIFILM DIMATI
RDUE UNIVERSITY • INTEL • ABB SEMICONDUCTO
NDUCTORS • WITRICITY • MEDTRONIC • PURDUE U

COMSOL

READ LATEST ISSUE »

Plasmonic core-shell gold nanoparticle enhanced optical absorption in photovoltaic devices

Di Qu (曲迪), Fang Liu (刘仿),^{a)} Jiafan Yu (于嘉钊), Wanlu Xie (谢婉露), Qi Xu (许骐), Xiangdong Li (李向东), and Yidong Huang (黄翊东)^{b)}
State Key Laboratory of Integrated Optoelectronics, Department of Electronic Engineering, Tsinghua University, Beijing 100084, People's Republic of China

(Received 29 November 2010; accepted 3 February 2011; published online 18 March 2011)

The enhancement effect of optical absorption with core-shell gold nanoparticles on the surface of wafer-based silicon photovoltaic devices has been studied. The obvious enhanced photocurrent is observed, especially when the wavelength is above 800 nm, and the highest enhancement value is about 14% around the wavelength of 1100 nm. The simulation results indicate that the presence of dielectric coating shell could improve the surface plasmon based scattering effect at longer wavelength range, which provides a good understanding of the experiment results. © 2011 American Institute of Physics. [doi:10.1063/1.3559225]

The enhanced optical absorption in solar cells using nanoscale structure and novel physical effect has received a lot of attention in recent years.¹ Utilizing noble metal nanoparticles with plasmonic effects is considered as one of the promising methods for increasing the light absorption, and consequently the conversion efficiency of photovoltaic devices.²⁻⁸ The nanoparticles had been applied not only on the front or on the rear of the active layer with the surface plasmon enhanced scattering effect²⁻⁷ but also inside the active layer with the local field enhancement effect near the metal nanoparticles.⁸ However, the plasmonic enhancement effect for increasing the conversion efficiency of photovoltaic devices may be limited when the bare metal nanoparticles are directly applied both outside and inside the active layer, because those nanoparticles could be the recombination centers for light-induced electrons and holes as mentioned in Refs. 4, 6, and 8. And the plasmonic related scattering and local field enhancement effect are hard to cover the whole wavelength range of silicon response spectrum by only varying the size and shape of the nanoparticles.^{4,6}

In this paper, we propose to apply the plasmonic metal-dielectric core-shell structure for increasing the conversion efficiency of solar cells. Here, the plasmonic Au-citrate core-shell nanoparticles are synthesized chemically and deposited on the surface of wafer-based silicon photovoltaic devices. The measurement results demonstrate that the enhanced photocurrent is obtained over almost the entire silicon response spectrum. The obviously enhanced photocurrent is observed above the wavelength of 800 nm. The highest value of photocurrent enhancement, as high as 14%, is realized at the wavelength of 1100 nm. Compared with the research results reported in Ref. 4, where gold nanoparticles were not coated by the dielectric surrounding, the enhancement effect is more obvious and moved to longer wavelength range. The reason could be a decrease in surface recombination induced by bare metal nanoparticles as well as an increase in scattering cross section at longer wavelengths, due to the presence of dielectric coating shell. Correspondingly, the numerical simulations have also been carried out to provide a good

understanding of our experimental results. Furthermore, we expect that varying the coating dielectric materials surrounding metal nanoparticles can effectively tune the wavelength of surface plasmon based enhancement effect, since the wavelength is sensitive to the metal dielectric environment.^{9,10}

Figure 1 shows the schematic diagram of the wafer-based silicon photovoltaic device with Au-citrate core-shell nanoparticles on the surface. The device is realized by applying the ion implantation method on a p-type Si wafer with 525 μm thickness to get the pn-junction and then fabricating the electrodes on both sides of the device.

The colloidal gold nanoparticles with core-shell structure are synthesized by the standard sodium citrate reduction method.¹¹ $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (SIGMA-ALDRICH, 99.0%) and sodium citrate (referred to as citrate, SIGMA-ALDRICH, 98.0%) are used as starting material and reducing agent, respectively. This simple method can produce a stable, purple solution of citrate coated gold nanoparticles, where citrate is an electrostatic stabilizing agent for gold nanoparticles¹² and as a result, can effectively avoid the surface recombination induced by the direct contact between metal and active material. The size of gold core and the thickness of citrate shell can be controlled by adjusting the ratio of HAuCl_4 and citrate, reactant concentration, reaction temperature and reaction time. Figure 2(a) shows the transmission electron microscope (TEM, JEOL 2010) photograph of an Au-citrate core-shell nanoparticle.

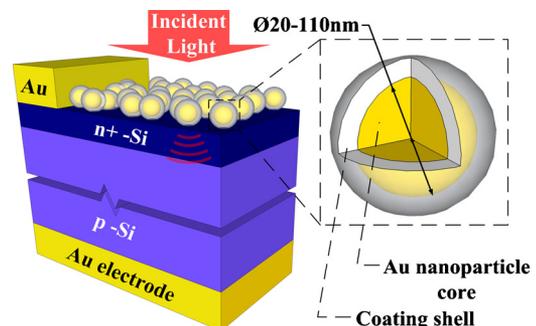


FIG. 1. (Color online) Schematic diagram of the photovoltaic device with Au-citrate core-shell nanoparticles on the top.

^{a)}Electronic mail: liu_fang@tsinghua.edu.cn.

^{b)}Electronic mail: yidonghuang@tsinghua.edu.cn.

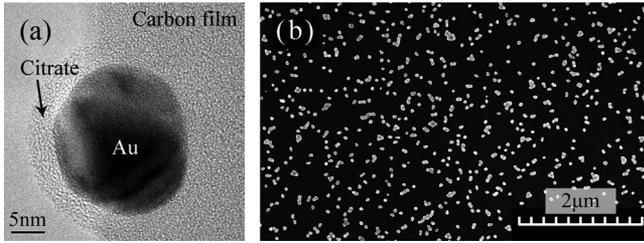


FIG. 2. (a) The photo of TEM showing an Au-citrate core-shell nanoparticle located at the edge of carbon film on the microgrid. (b) The photo of SEM showing the Au-citrate core-shell nanoparticles deposited on the device surface.

Then, by dropping the solution of Au-citrate core-shell nanoparticles directly on the surface of the photovoltaic device and drying the sample, the fabrication of the device is finished. Figure 2(b) is the photograph of the core-shell gold nanoparticles deposited on the device surface under scanning electron microscope (SEM, HITACHI S-5500). It is shown that the size of nanoparticles is in the range of 20–110 nm, the concentration is about $1.9 \times 10^9 \text{ cm}^{-2}$, and the surface coverage is about 12%. Meanwhile, some photovoltaic devices without covering core-shell gold nanoparticles are remained in the same wafer for comparison with the devices with nanoparticles.

The photocurrent response spectra of the silicon photovoltaic devices (with and without Au-citrate core-shell nanoparticles) are measured by the standard solar cell relative spectral response measurement system,¹³ which includes a tungsten-halogen lamp (OSRAM), a grating monochromator providing monochromatic light, a filter wheel for the elimination of multispectral, a reference Si photodiode, a Si photodetector, and a lock-in amplifier. With this system, the photocurrent response of the device under different wavelength (from 300 to 1800 nm) can be obtained with high measurement repeatability (the error <1%).

Figure 3 shows the measured photocurrent response ratio (I_{ph} ratio) of photovoltaic devices with and without Au-citrate core-shell nanoparticles as a function of wavelength. For each curve, four groups of samples have been measured and the average value and error bar are illustrated. Figure 3(a) shows the results of the samples with gold nanoparticles size mainly within the range of 60–110 nm. It can be seen that the enhancement on photocurrent response is obtained

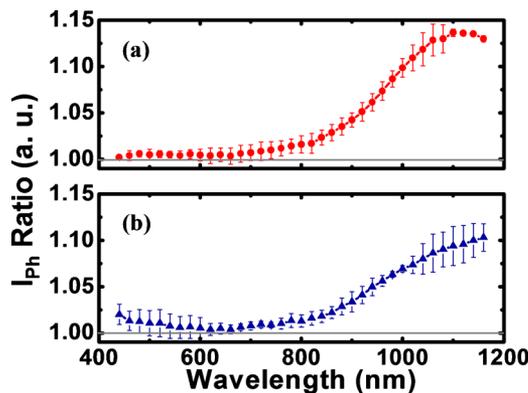


FIG. 3. (Color online) Measured photocurrent response ratio (I_{ph} ratio) of four groups of devices with and without Au-citrate core-shell nanoparticles as a function of wavelength. Nanoparticles' sizes mainly range (a) from 60 to 110 nm and (b) from 20 to 70 nm.

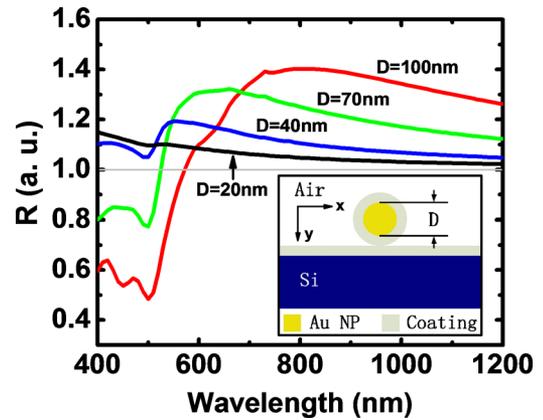


FIG. 4. (Color online) The simulation result of enhancement ratio (R) with and without Au-citrate core-shell nanoparticles as a function of wavelength. The inset shows the schematic diagram of the simulation geometry.

over almost the entire silicon response spectrum. There is a notable increase when the wavelength of incident light $\lambda_0 > 800 \text{ nm}$, and the increase reaches 14% around $\lambda_0 = 1100 \text{ nm}$. In Fig. 3(b), when decreasing the average size of gold nanoparticles (mainly within the range of 20–70 nm) by adjusting the ratio of reactants ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and citrate), similar enhancement results have also been derived with lower enhancement values at longer wavelengths due to the size effect.^{2,4}

This improvement results from the enhanced scattering effect of incident light with plasmonic core-shell gold nanoparticles. Compared with the results reported in Ref. 4, where the similar technique method was adopted, the enhancement is more obvious and occurs at longer wavelength range in our experiment. This is because the citrate surrounding gold nanoparticles changes the local dielectric environment of surface plasmon resonance, which leads to a redshift of surface plasmon resonance wavelength^{7,10} as well as an increase in scattering cross section at longer wavelengths. Meanwhile, the citrate shell could avoid the surface recombination induced by bare metal nanoparticles, which could decrease the photocurrent response, especially in the shorter wavelength region.^{4,14} Furthermore, silver can be used in the metal-dielectric core-shell structure to avoid oxidation, which would have better performance than gold.

To understand the above results more clearly, the RF module of the software COMSOL MULTIPHYSICS[®] is adopted to simulate a model in two-dimension. As shown in the inset of Fig. 4, a metal-dielectric core-shell nanoparticle is located on the Si layer, where the diameter of the gold core D is variable and the thickness of the coating shell is fixed at 10 nm. The periodic boundary conditions in x -direction are applied for considering the multiple scattering and cross-coupling between neighboring nanoparticles. And the periodicity of 230 nm in the x -direction corresponding to a nanoparticle density of $1.89 \times 10^9 \text{ cm}^{-2}$ is consistent with the actual concentration in our experiment. A plane wave propagating along y -direction with unity amplitude is introduced at the top boundary. By the way, the material dispersion of Au and Si has been considered.¹⁵

As the photocurrent is proportional to the light absorption in the silicon, the increase in the light characterized as the electric field intensity could be considered as the increase in the photocurrent in the photovoltaic device. Therefore, the

ratio (R) of the light propagating into the silicon region for the model with and without core-shell nanoparticles could be considered as the ratio of photocurrent responses in the experiment,⁴ which means that the vertical axes of Figs. 4 and 3 are equivalent. It is obvious that the peak value of R increases and redshifts with the size of nanoparticles, owing to the larger surface plasmon enhanced scattering cross section at longer wavelength range. The dip for each curve when λ_0 is about 500 nm results from the backward scattering and the excitation of localized surface plasmon resonance of nanoparticles.⁴ Although the actual situation (nanoparticles within a size range are randomly distributed) is more complicated than the simulation model, it can be noticed that the experiment and simulation results have the same trends by comparing the curves of Figs. 3 and 4. First, the enhancement effect is more obvious in the longer wavelength region. Second, the larger nanoparticle size corresponds to the higher enhancement value.

In conclusion, enhanced optical absorption by applying the plasmonic core-shell gold nanoparticles on the top of wafer-based silicon photovoltaic devices has been investigated experimentally and numerically. The obvious photocurrent enhancement is observed when the wavelength of incident light is above 800 nm. The highest enhancement, as high as 14%, is obtained around the wavelength of 1100 nm. And the simulation results help us understand the increasing photocurrent performance in the near-infrared wavelength range in the experiment. Considering the poorly optical absorption of thin film absorber materials, the efficiency enhancement based on plasmonic metal-dielectric core-shell nanoparticles would be more obvious for thin film solar cells and detectors.

The authors would like to acknowledge Limin Xiong and Hao Sun of National Institute of Metrology, China, for their advice and help in measurement. This work was supported by the National Basic Research Programs of China (973 Program) under Contract Nos. 2011CB301803, 2007CB307004, and 2006CB302804, and the National Natural Science Foundation of China (Grant Nos. NSFC-61036011 and NSFC-60877023).

¹H. A. Atwater and A. Polman, *Nature Mater.* **9**, 205 (2010).

²D. M. Schaadt, B. Feng, and E. T. Yu, *Appl. Phys. Lett.* **86**, 063106 (2005).

³D. Derkacs, S. H. Lim, P. Matheu, W. Mar, and E. T. Yu, *Appl. Phys. Lett.* **89**, 093103 (2006).

⁴S. H. Lim, W. Mar, P. Matheu, D. Derkacs, and E. T. Yu, *J. Appl. Phys.* **101**, 104309 (2007).

⁵P. Matheu, S. H. Lim, D. Derkacs, C. McPheeters, and E. T. Yu, *Appl. Phys. Lett.* **93**, 113108 (2008).

⁶S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, *J. Appl. Phys.* **101**, 093105 (2007).

⁷F. J. Beck, A. Polman, and K. R. Catchpole, *J. Appl. Phys.* **105**, 114310 (2009).

⁸B. P. Rand, P. Peumans, and S. R. Forrest, *J. Appl. Phys.* **96**, 7519 (2004).

⁹A. Polman, *Science* **322**, 868 (2008).

¹⁰G. Xu, M. Tazawa, P. Jin, S. Nakao, and K. Yoshimura, *Appl. Phys. Lett.* **82**, 3811 (2003).

¹¹B. V. Enustun and J. Turkevich, *J. Am. Chem. Soc.* **85**, 3317 (1963).

¹²S. H. Brewer, W. R. Glomm, M. C. Johnson, M. K. Knag, and S. Franzen, *Langmuir* **21**, 9303 (2005).

¹³The solar cell relative spectral response measurement system of the National Institute of Metrology (NIM, China) is for calibrating the characteristics of solar cells.

¹⁴S. M. Sze, *Physics of Semiconductor devices* (Wiley, New York, 1981), Chap. 14.

¹⁵E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, Orlando, 1985), pp. 286–295 and pp. 547–569.