Journal of the Korean Physical Society, Vol. 56, No. 5, May 2010, pp. 1488∼1491

Localized Surface Plasmon Resonances Caused by Ag Nanoparticles on SiN for Solar Cell Applications

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(Received 4 March 2010, in final form 27 March 2010)

This study examined experimentally and theoretically the coupling of metal (Ag) localized surface plasmon resonances (LSPRs) and a dielectric (SiN) layer to enhance the photovoltaic properties of Si solar cells. The coupling of metal LSPRs and a SiN layer enhanced the intensity and optimized the projection of the internal electromagnetic field induced by the metal LSPRs. Therefore, the overall backscattering and dissipation of light absorption over 400 - 1400 nm were suppressed, resulting in an increase in the photovoltaic conversion efficiency. The mechanism of the coupling of Ag LSPRs and the SiN layer was examined by using a finite element numerical simulation and experiments.

PACS numbers: 72.10.-d, 73.20.Mf, 88.40.Jj
Keywords: Localized surface plasmon resonance, Dielectric, Silicon, Solar cell
DOI: 10.3938/jkps.56.1488

I. INTRODUCTION

Si solar cells are promising candidates for large-scaled sunlight photovoltaic conversion [1–4]. However, Si solar cells require thick layers (>100 μm) to obtain effective absorption of the near infrared radiation due to the indirect band gap of crystalline Si. This increases the manufacturing costs and energy payback time due to the limited carrier diffusion length [5]. Localized surface plasmon resonances (LSPRs), which optically enhance light absorption because of enlarged optical cross sections, have been studied extensively in an attempt to enhance the photovoltaic conversion efficiency of thin film solar cells [2–4]. However, depending on the incident light's wavelength and the particle-substrate coupling, the LSPRs formed by metal particles attached to a photoactive substrate both reduce and enhance the photovoltaic carrier generation [5], as interpreted by various experimental and simulation models [5,6]. This has considerable drawbacks for LSPR anti-reflection coatings (ARC) due to the increased light reflection in the short-wavelength range of 400 - 600 nm for a thin semiconductor substrate [7–9].

In this study, the coupling effects of metal (Ag) LSPRs and a SiN layer were examined using a finite element calculation and experimental measurements. The coupling of Ag LSPRs and SiN largely enhances the intensity and effectively optimizes the projection of the internal electromagnetic field induced by the LSPRs. As a result, the optical cross-sections of the LSPRs are enlarged considerably with the concomitant suppression of backscattering. Therefore, the Ag LSPRs on SiN enhance light absorption in Si solar cells over the entire wavelength range of 300 - 1400 nm. The morphology of metal nanoparticles and the thickness of the dielectric layer can be engineered to optimize the level of light absorption. Using Ag LSPRs on SiN, the efficiency of Si solar cells can be enhanced by 0.9%, 3.3%, and 9.9% compared to that of Si solar cells with a SiN ARC, Ag LSPRs on Si, or a textured bare Si surface, respectively.

II. SIMULATION AND EXPERIMENTAL RESULTS

Ag LSPRs cause oscillations of electrons in confined geometries. The movement of the conduction electrons up to excitation by the incident light leads to a build up of polarization charges on the LSPR surface, and the resulting electromagnetic field behaves as a restoring force allowing the LSPRs to occur at a particular (photon) frequency [6]. The resulting internal electromagnetic field can be expressed as $E_i = E_o 3\epsilon_d \ / \ (\epsilon_m + 2\ \epsilon_d)$, where E_o is the reference internal field and can be obtained

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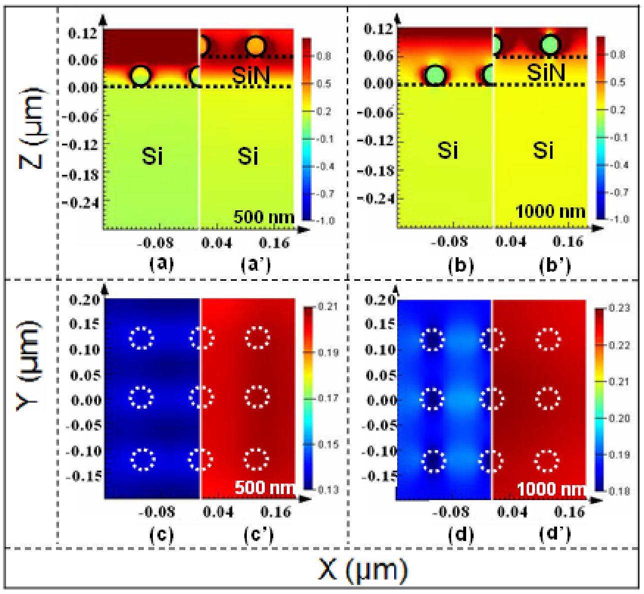

Fig. 1. Three-dimensional illustrations of the internal electric field at different wavelengths near the LSPRs along the (Z - X) axis for the cross section and the (Y - X) axis extending normal to the surface. The amplitude is relative to the field calculated for an individual Ag LSPR with a diameter of 35 nm with (a'-d') and without (a-d) a 65-nm-thick SiN layer on p-type Si. The incident wavelengths were 500 nm in (a,a',c,c') and 800 nm in (b,b',d,d').

experimentally, and ϵ_d and ϵ_m are the permittivities of the substrate (dielectric) and the metal LSPRs, respectively. A strong interaction of LSPRs with the incident field occurs at incident light frequencies that induce ϵ_m = -2ϵ_d, with $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$ according to the polarity of the incident photons [9]. The coupling of metal LSPRs and a dielectric substrate might affect the optical and the electrical properties of metal LSPRs.

To better understand the coupling effects of Ag LSPRs and a SiN layer, we performed a finite element numerical simulation by solving the three-dimensional (3D) vector Helmholtz equation in the frequency domain for a scattered electric field at normal incidence (see Appendix II in Ref. 10). Figure 1 shows the simulation results for the internal field induced by spherical Ag LSPRs (with a diameter of 35 nm) on a Si substrate (a-d) and on a 65-nm-thick SiN layer (a'-d'). At the main resonance (∼500 nm, for the LSPRs with a diameter of 35 nm), the internal field induced by the LSPRs on SiN was largely enhanced and confined between the LSPRs and the SiN layer. The internal field rarely spreads to the photovoltaic substrate (Si), which suppresses the backscattering of light in the Si substrate, as shown in the 3D illustration in Figs. 1(a') and 1(c'). In contrast, without a SiN layer between the Ag LSPRs and the Si substrate, the internal field induced by the LSPRs is projected mainly to the Si substrate, inducing considerable backscattering of light, as shown in Figs. 1(a) and 1(c). On the other hand, the LSPRs

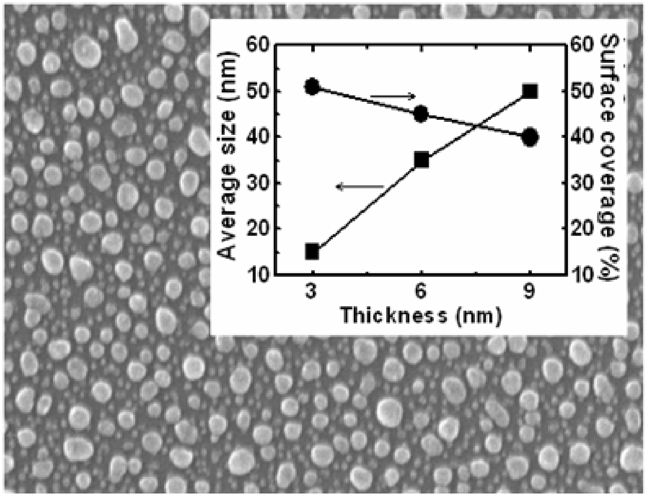

Fig. 2. Surface SEM image of the Ag NPs with an average diameter of ∼15 nm on SiN on a planar Si surface, and (inset) the average diameters of the Ag NPs versus the thicknesses of the Ag films.

show strong resonance to incident light in the long wavelength range, *e.g.*, 800 nm [5]. The internal field mainly spreads along the Z-X axis when the LSPRs are on SiN, enlarging the optical capture cross-sections and enhancing light absorption, as shown in Figs. 1(b') and 1(d') [5]. In contrast, without the SiN layer between the Ag LSPRs and the Si substrate, the internal field induced by the LSPRs spreads along the Z-X axis and is projected to the Si substrate along the Y-X axis. The combined effect of forward scattering and backscattering occurs on the photovoltaic substrate. Although the net effect may still enhance light absorption and the solar cell efficiency, the effects of such metal LSPRs are not completely understood [5], as shown in Figs. 1(b) and 1(d). Therefore, a SiN layer between the Ag LSPRs and the Si substrate is expected to (i) greatly enhance the internal field near the LSPRs, and (ii) effectively optimizes the internal field projections due to the metal LSPRs on the dielectric architecture for solar cell efficiency enhancement.

The particle size has a strong influence because the electric field is enhanced by larger sized LSPRs, and the electric field is proportional to the absorption cross section [6]. Therefore, larger sized LSPRs will provide better photon absorption. This is consistent with the reported theory, in which the photon absorption cross section is given as $C_{abs} = \frac{2\pi}{\lambda}\mathrm{Im}[\alpha]$, where $\alpha = 3V\left(\frac{\varepsilon_m - 1}{\varepsilon_m + 2}\right)$, λ is the wavelength, and V is the volume of the LSPRs [9]. Nevertheless, the photon reflection cross section is also enlarged as $C_{sca} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4|\alpha|^2$ for larger-sized LSPRs [9]. Therefore, proper-sized LSPRs, *e.g.*, with an average diameter of ∼35 nm, can result in optimal efficiency.

The optical and the electrical efficiencies of Si solar cells with Ag LSPRs on a SiN structure were examined

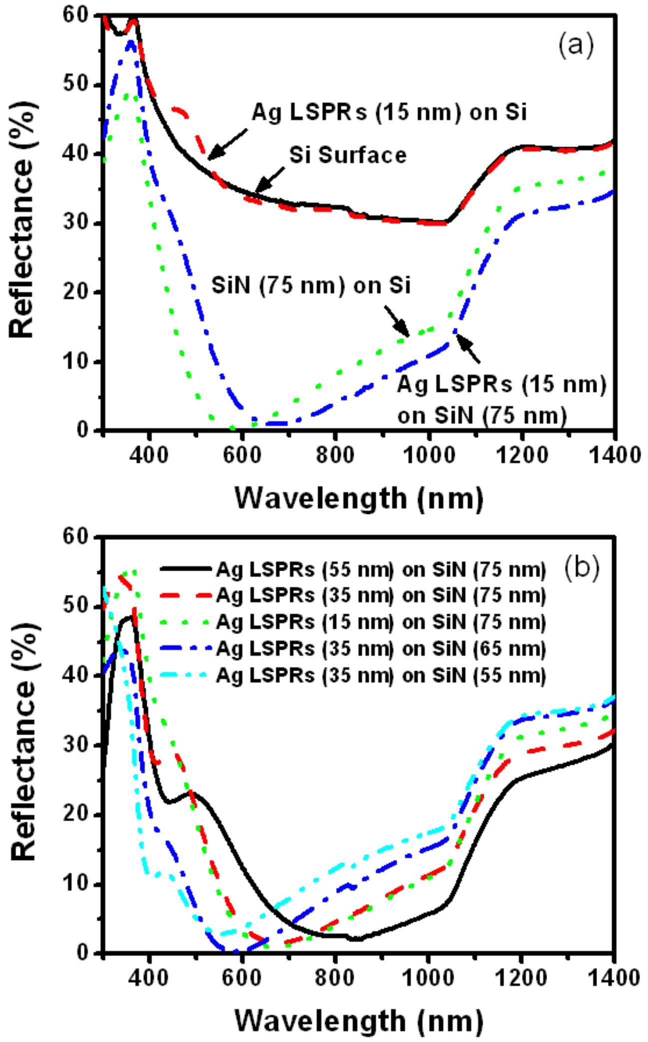

Fig. 3. (a) Photon reflectance of the Si surface, Si with a SiN ARC, Si with Ag NPs on surface, and Si with Ag NPs on a SiN structure. (b) Optimization of the antireflection properties of the Ag NPs on the SiN structure by engineering the morphology of the Ag NPs and the thickness of the SiN.

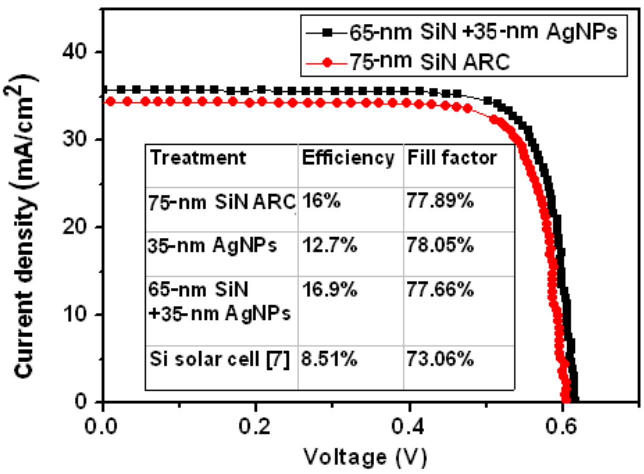

Fig. 4. I-V characteristics of Si PVCs with only a SiN ARC and with Ag NPs on the ARC structure.

experimentally. Ag films with various thicknesses (3 / 6 / 9 nm) were deposited by electron beam evaporation at room temperature on SiN layers with different thicknesses (∼55 nm / ∼65 nm / ∼75 nm) on a (110) Si wafer. After annealing at 200 °C for 1 hour, the Ag LSPRs were formed [2–4]. The average diameters of the 3-, 6-, and 9-nm-thick LSPRs were ∼15 nm, ∼35 nm, and ∼55 nm, respectively, according to high-resolution scanning electron microscopy (SEM). Figure 2 shows a SEM image of the SiN surface with ∼15-nm Ag LSPRs. The inset presents the average diameters of the Ag LSPRs as a function of the thicknesses of the pre-deposited Ag film's transient. An UV/VIS spectrophotometer was used to detect the light reflectance of the Ag LSPRs on SiN in the wavelength range of 300 - 1400 nm. Figure 3(a) shows the reflectance of the Ag LSPRs with an average diameter of ∼15 nm on a 75-nm-thick SiN layer as a function of the wavelength. The Ag LSPRs suppress photon reflection by ∼1% - 3% when they are deposited on the Si surface while they suppress light reflection by ∼5% - 6% on SiN in the wavelength range of 800 - 1400 nm. On the other hand, light reflection is enhanced by ∼5% - 9% for the Ag LSPRs on Si over the wavelength range of 400 - 600 nm. Such enhanced reflection is suppressed for the Ag LSPRs on SiN. The total reflectance over the wavelength range of 300 - 1400 nm can be optimized by engineering the diameter of the Ag LSPRs and the thickness of the SiN layer, as shown in Fig. 3(b). For example, the reflectances of the Ag LSPRs with average diameters of ∼15 nm, ∼35 nm, and ∼55 nm on a 75-nm-thick SiN were reduced by ∼5%, ∼7%, and ∼10% over the wavelength range of 800 - 1400 nm, compared to that of a 75-nm-thick SiN without the Ag NPs in Fig. 3(a). Although larger-sized LSPRs reduce the photon reflectance more effectively in the wavelength range of 800 - 1400 nm, they also enhance photon reflectance more drastically over the wavelength range of 400 - 600 nm [7–9]. LSPRs with a diameter of ∼35 nm suppress the reflectance more effectively than those with a diameter of ∼15 nm while the ∼35-nm LSPRs do not enhance the reflectance significantly compared to the ∼15 nm LSPRs, as shown in Fig. 3(b). The total reflectance of the ∼35-nm LSPRs was minimized compared to those of the ∼15 nm and ∼55 nm LSPRs. On the other hand, the total reflectance of the ∼35 nm LSPRs can be optimized further by engineering the thickness of the SiN layer. LSPRs, ∼35 nm in size, on a 65-nm-thick SiN layer may suppress the total reflectance more effectively than those on a 75-nm-thick SiN layer. However, a too thin, *e.g.*, 55-nm-thick, SiN may be insufficient to suppress the reflectance in both the long (800 - 1400 nm) and the short (400 - 600 nm) wavelength ranges, as shown in Fig. 3(b).

The photovoltaic properties of Si solar cells with Ag LSPRs on a SiN structure were examined using a Gamry

FAS1 potentiostat under a polarization- and bandpass-filtered (400 - 1400 nm and 10-nm full width at half maximum) Xe arc lamp. The solar illumination was provided by a solar simulator under AM1.5 illumination. The total electrical efficiency of Si solar cells with the ∼35-nm Ag LSPRs on the 65-nm-thick SiN was compared with those of Si solar cells with only a 75-nm-thick SiN (which is the optimum condition for an ARC) and with only ∼35-nm Ag LSPRs on the Si surface of the Si solar cells. Figure 4 shows the I-V characteristics of Si PVCs with only a 75-nm SiN ARC and with 35-nm Ag NPs on a 65-nm ARC structure. The electrical efficiency of the Si solar cells with the Ag LSPRs on the SiN structure was greatly enhanced (16.9%), compared to that with only an 75-nm-thick SiN ARC (16%) or with only the Ag LSPRs (12.7%). Note that the efficiency of Si solar cell with no ARC or no surface texture may be as little as 8.51% [7].

III. CONCLUSION

In summary, this study examined the coupling effects of Ag LSPRs and a Si layer. A SiN layer between the Ag LSPRs and a photoactive substrate effectively increases the Si solar cell efficiency by enhancing the generation of the internal field and by effectively optimizing the projection of the internal field. The materials, the morphology of the metal (Ag) LSPRs, and the thickness of the dielectric (SiN) layer can be engineered to further improve the efficiency of a Si solar cell.

REFERENCES

[1] M. A. Green, Prog. Photovoltaics **14**, 383 (2006).

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

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

[4] H. R. Stuart and D. G. Hall, Appl. Phys. Lett. **73**, 3815 (1998).

[5] C. Hagglund, M. Zach, G. Petersson and B. Kasemo, Appl. Phys. Lett. **92**, 053110 (2008).

[6] W. L. Barnes, A. Dereux and T. W. Ebbesen, Nature **424**, 824 (2003).

[7] T. L. Temple, G. D. K. Mahanama, H. S. Reehal and D. M. Bagnall, Sol. Energy Mater. Sol. Cells **93**, 1978 (2009).

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

[9] S. Pillai, Ph. D. dissertation, the University of New South Wales, 2007.

[10] EPAPS document No. E-APPLAB-92-036806 (http://www.aip.org/pubservs/epaps.html).