Improved multicrystalline Si solar cells by light trapping from Al nanoparticle enhanced antireflection coating

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Abstract: Significant photocurrent enhancement of 0.4 mA/cm^2 has been achieved for industrial textured multicrystalline silicon solar cells, due to the light trapping provided by aluminium nanoparticle enhanced antireflection coating. Aluminium nanoparticles support surface plasmon resonances, which can effectively scatter the light into the solar cells. By blue shifting the detrimental Fano resonances away from the important silicon absorption spectrum, aluminium nanoparticles can provide a broadband light absorption enhancement without a reduction at the short wavelengths. Combining the discovery with 75 nm silicon nitride antireflection coating, which can significantly enhance the absorption at the peak solar spectrum, we have achieved the strong broadband light absorption enhancement.

OCIS codes: (160.4236) Nanomaterials; (310.6628) Subwavelength structures, nanostructures; (250.5403) Plasmonics; (040.5350) Photovoltaic.

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1. Introduction

Multicrystalline Si (mc-Si) solar cells have taken the position of single crystalline Si (sc-Si) solar cells and become the market-dominating technology, due to the relatively low cost [1]. However, the energy conversion efficiencies of the mc-Si solar cells are lower, mainly due to the ineffective light trapping scheme. The light trapping in sc-Si solar cells is almost perfect in the whole silicon absorbing wavelengths ranging from 300 nm to 1200 nm, due to the combination of the pyramid textured surface and a SiN_x antireflection coating (ARC) [2]. However, effective pyramid textured surface structures cannot be formed on mc-Si solar cells through the conventional chemical etching method due to the different crystal orientations on the mc-Si surface [3]. As a result, a higher reflectance at both the shorter and longer wavelengths is presented leading to the poor light trapping in these wavelength regimes, which has remained as a key challenge limiting the energy conversion efficiency of mc-Si solar cells.

Metallic nanoparticles, which support localized surface plasmon resonances, have been demonstrated to be able to enhance the light trapping in solar cells and the internal quantum efficiency due to the ability for tuning Purcell factor in engineered surface plasmon structures [4–18]. The tuning of surface plasmon frequency had been reported by using metallic nanoparticles with various dimensions [17], and multi-layered plasmonic structures [18]. These approaches had been shown to result in engineering of Purcell factor in various spectral regimes leading to improved internal quantum efficiencies in radiative and absorption processes in semiconductor quantum wells. Among the different materials of metallic nanoparticles, noble metals such as Ag and Au have been investigated on thin film solar cells. However, Fano effect is a fundamental limitation for the noble metallic nanoparticles when integrating with solar cells [14]. In addition, noble metals are inherently inappropriate for practical device applications. Al was theoretically predicted to be superior than the most

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widely used noble nanoparticles (Ag and Au) in enhancing the light trapping in crystalline Si solar cells due to the less reduction of the light trapping in the shorter wavelengths below the plasmonic resonance [14]. Together with the low cost advantage, Al nanoparticles hold the great promise for large scale integration and dramatic improvement of the light trapping in mc-Si solar cells.

In this paper, we first investigated the fundamental effect induced solely by the Al nanoparticles through integrating the nanoparticles on the top surface of planar mc-Si solar cells without the SiN_x ARC (bare cell). Then the Al nanoparticles were integrated on the surface of the SiN_x layer on a planar mc-Si solar cell, forming a hybrid Al nanoparticle/SiN_x ARC to enhance the light transmittance into the Si. Finally, the nanoparticles were incorporated on the top surface of the industrial standard textured mc-Si solar cells, which is of practical importance for the photovoltaic industry.

2. Experimental and simulation methods

The 180 μm planar mc-Si solar cells were fabricated by the following processes. Saw damaged surfaces of the p-type (boron doped) mc-Si wafers were first etched off by dipping the wafers into the HNO_3/HF solution. After the standard RCA cleaning (as developed at Radio Corporation of America) process, the n^+ emitters with a sheet resistance around 100 $\Omega/\square$ were formed by the diffusion of the $POCl_3$ source at the temperature around 850 °C. The phosphosilicate glass introduced by the diffusion process was removed by the HF solution. Then Al paste was screen printed on the rear surface and fired at a temperature around 800 °C for a few seconds to form the back surface field (BSF). A 2 μm thick Al top contact grid was formed by the photolithography. After that, the SiN_x ARC was deposited by the plasmon-enhanced chemical vapour deposition (PECVD) system at 350 °C. The standard textured mc-Si solar cells with a thickness around 180 μm were supplied by Suntech Power Holdings Co., Ltd.

To produce controlled Al nanoparticles with high reproducibility, a 10 nm Al film was evaporated on the NaCl powder substrate, followed by a high temperature annealing process. Then the powder was dissolved in deionized water and Al was separated from the water solution by centrifuge. The prepared Al nanoparticles were integrated on the top surface of the solar cells by drop casting.

Figure 1 shows the schematic structures of the mc-Si solar cells investigated in this work, including (a) Al nanoparticles on the bare cell, (b) Al nanoparticles on the planar cell with a 75 nm SiN_x ARC and (c) Al nanoparticles on the standard cell with both the textured surface and the SiN_x ARC. The nanoparticles are uniformly distributed on the Si wafers over a large surface area as shown in the SEM image of Fig. 1(d). It is clear that the shape of the nanoparticles is sphere with a statistically averaged diameter around 100 ± 30 nm.

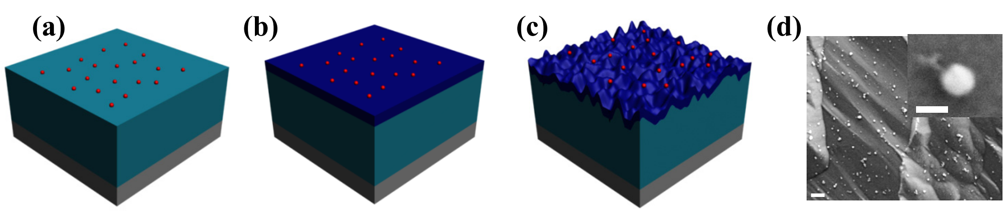

Fig. 1. Schematics of the Al nanoparticles on the top surface of different solar cell structures: (a) bare solar cells, (b) planar solar cells with a 75 nm SiN_x ARC, (c) standard solar cells with both the textured surface and the SiN_x ARC and the corresponding SEM image (d) of the Al nanoparticles on the surface of a planar silicon wafer (scale bar: 1 μm). The inset SEM shows the Al nanoparticle in large magnification with a scale bar of 100 nm. Red: Al nanoparticles; dark blue: SiN_x ARC; light blue: Si wafer; grey: Al rear contact.

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Reflectance and external quantum efficiency (*EQE*) measurements were performed before and after the nanoparticle integration. The short circuit current density (J_{sc}) was calculated by the following equation:

$$J_{sc} = q\int \frac{\lambda}{hc} EQE(\lambda) I_{AM1.5} d\lambda, \tag{1}$$

where q is the electron charge, λ is the wavelength of the light in free space, h is Planck's constant, c is the speed of light in free space, $EQE(\lambda)$ is the *EQE* at the wavelength λ and $I_{AM1.5}$ is the standard solar spectrum (Air Mass 1.5 global, AM1.5G). The finite difference time domain (FDTD) method was employed to simulate the light reflectance and transmittance into the Si wafer induced by the Al nanoparticles [19]. Perfectly matched layer boundary conditions were used in the incident direction to prevent the interference effect and periodic boundary conditions were used in the lateral direction to simulate an ordered array of nanoparticles.

3. Results and discussion

To solely investigate the light trapping properties of the Al nanoparticles at the air/Si interface and exclude the interruption of other light trapping effects from the textured surface and ARC, we perform the experiments and simulations of Al nanoparticles on the bare solar cells. Figure 2(a) shows that the Al nanoparticles can effectively reduce the reflectance and increase the *EQE* of the bare mc-Si solar cells in the whole silicon absorption wavelength range. By integrating the experimentally measured *EQE* with the standard AM1.5G solar spectrum, the J_{sc} value rises from 23.7 mA/cm^2 to 24.7 mA/cm^2 with an enhancement of 4% due to the light trapping effect of the Al nanoparticles. It is interesting to note that the *EQE* enhancement is broadband over the entire spectrum with an up to 40% enhancement at the short wavelengths. This is distinctive to other widely used Ag and Au nanoparticles, in which the *EQE* was found to reduce at the short wavelengths [20,21]. This reduction occurs due to the Fano effect, i.e., the destructive interferences between the scattered and unscattered light below the surface plasmon resonance [22]. For the Al nanoparticles, the Fano resonance is blue shifted to the wavelengths below the solar spectrum edge at 300 nm, and therefore become harmless to the performance of the solar cells. Figure 2(b) shows the simulation results on mc-Si solar cells, where the trends for the reflectance reduction and the transmittance enhancement are in line with the experimental results in Fig. 2(a). The simulation is based on the averaged diameter 100 nm of the Al nanoparticles and a periodical array on the Si surface with a coverage density around 10%. The appreciable difference in the longer wavelengths above 1000 nm is due to the semi-infinite consideration in the simulation, which excludes the influence of the reflected light from the rear surface so that the antireflection effect of the front surface can be investigated separately. It is confirmed that the enhancement mainly comes from the front surface antireflection effect for 180 µm Si wafer. Therefore, the semi-infinite consideration is valid. Additionally, the non-periodical nanoparticle array in experiment can also be responsible for the difference between the simulated and experimental results.

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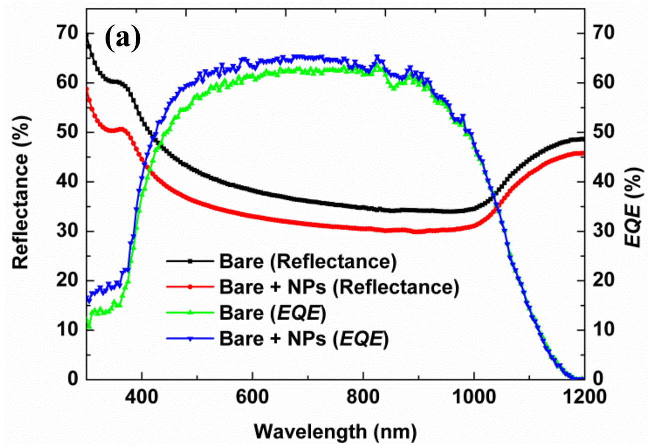

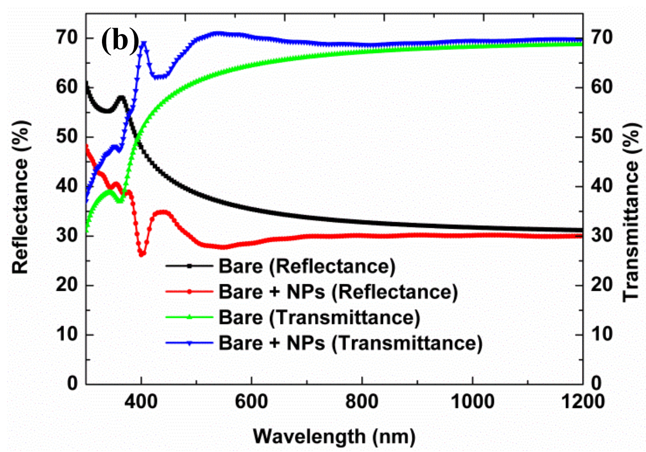

Fig. 2. (a) Experimentally measured light reflectance and external quantum efficiency (*EQE*) of the bare mc-Si solar cells with and without the 100 nm Al nanoparticles (NPs) on the top surface. (b) FDTD simulation results of the light reflectance and transmittance of the bare Si with and without the 100 nm Al NPs on the top surface of the Si.

In crystalline Si solar cells, the SiN_x ARC is widely used to reduce the light reflection and increase the *EQE* by the mechanism of the destructive interference. However, since the interference is sensitive to the wavelength of the light, the reflection minima can only be achieved in a relatively narrow spectral range at an optimized SiN_x thickness of 75 nm, which corresponds to the peak intensity of the solar spectrum around the wavelength of 600 nm. As investigated above, the Al nanoparticles can provide a broadband light absorption enhancement in Si, although the enhancement factor is relatively small, compared with the light absorption enhancement at the wavelengths around 600 nm for the optimized 75 nm SiN_x ARC. Considering the distinctive features of the two light trapping mechanisms, we integrated the Al nanoparticles on the top surface of the SiN_x to achieve the strong broadband light trapping. Figure 3 shows the experimental measured *EQE* enhancement of the bare mc-Si solar cells integrated respectively, with the Al nanoparticles, a 75 nm SiN_x ARC and the hybrid Al nanoparticle/SiN_x ARC. The *EQE* enhancement by the hybrid structure is larger than that with the Al nanoparticles or the SiN_x individually. Compared with that with the SiN_x ARC alone, the *EQE* of the hybrid structure was increased at both the shorter wavelengths below 400 nm and the long wavelengths above 700 nm, although there is a slight decrease at the visible wavelength region from 500 to 700 nm. The shorter wavelength enhancement is due to the forward scattering of the Al nanoparticles, which suppresses the relatively high

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reflectance from the SiN_x ARC, while the longer wavelength enhancement is a result of the red-shift of the SiN_x combined with the forward scattering by the Al nanoparticles. The middle wavelength reduction comes from the blocking of light from the Al nanoparticles. The total J_{sc} value rises from 35.0 mA/cm^2 to 35.5 mA/cm^2.

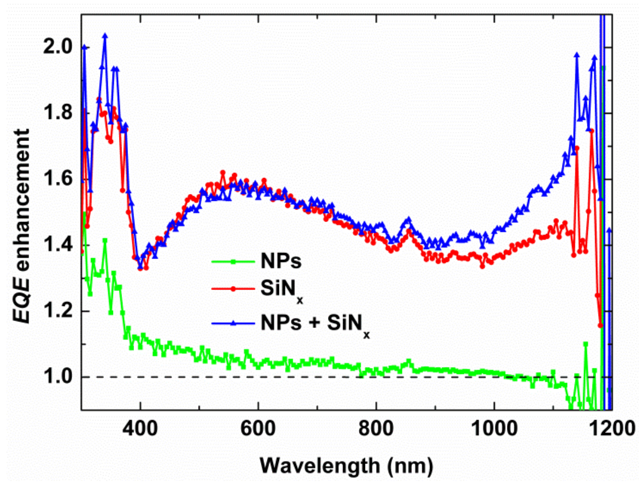

Fig. 3. Enhancement of the experimental external quantum efficiency (*EQE*) for the bare mc-Si solar cells with three light trapping schemes on the top surface: (i) Al nanoparticles alone (ii) SiN_x antireflection coating (ARC) alone and (iii) Al nanoparticle + SiN_x ARC hybrid structure.

On the specially fabricated planar mc-Si solar cells, the light trapping mechanism of the Al nanoparticle enhanced ARC is understood and the Al nanoparticle enhanced SiN_x ARC was demonstrated to outperform the conventional optimized SiN_x ARC in enhancing the light absorption in Si. Therefore, it provides a simple and low cost strategy to compensate for the ineffective light trapping of textured surface in mc-Si solar cells. We integrate the Al nanoparticles on the top surface of industrial standard textured mc-Si solar cells (Suntech Power Holdings Co., Ltd.), with the experimental results shown in Fig. 4. Clear *EQE* enhancement and reflectance reduction at the shorter wavelengths from 300 to 500 nm and the long wavelengths from 700 to 1200 nm were observed. The J_{sc} value was increased from 33.6 mA/cm^2 to 34.0 mA/cm^2. The same J_{sc} enhancement was also observed from the current-voltage (*I-V*) characterization, with the energy conversion efficiency rising from 14.2% to 14.5%. The enhancement trends of *EQE* and J_{sc} found on the textured mc-Si solar cells (Fig. 4) are similar to the trends found on the planar cells (Fig. 3). This indicates that a light trapping design at the nano-scale and another one at the micro-scale, which obey with different enhancement mechanisms, can be combined together on the same device to achieve even larger enhancements. The positive results provide a low cost solution to the solar cell industry.

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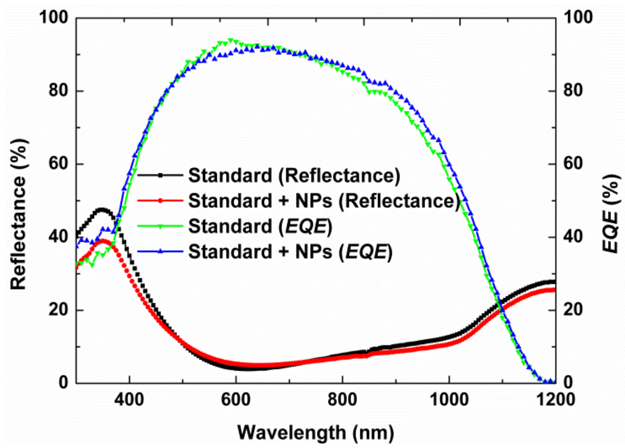

Fig. 4. Experimental reflectance and external quantum efficiency (*EQE*) of the standard textured mc-Si solar cells with and without the Al nanoparticles integrated on the top surface of the SiN_x ARC.

It is predicted by our simulations that the enhancement of the short circuit current density J_{sc} can be as high as around 1 mA/cm^2 for solar cells with the SiN_x ARC. The differences between experiments and simulations can be attributed to the non-ideal shape and size of the nanoparticles, and the deviation of the uniformity and coverage density of the nanoparticles distribution on the surface of the solar cells from the simulation. To further increase the short circuit current density J_{sc}, the integration method of the nanoparticles should be properly chosen and optimized. The current proof-of-concept experiment is based on drop casting method in achieving the deposition of Al nanoparticles. However, it is important to note that the other methods, such as rapid convective deposition [23–26] had been shown to result in high quality particle depositions on a large area wafer scale.

4. Conclusion

In conclusion, we have found the broadband *EQE* enhancement of the Al nanoparticles on the bare mc-Si solar cells and demonstrated the hybrid Al nanoparticle/SiN_x ARC, which outperforms the conventional optimized SiN_x ARC. More importantly, this hybrid structure effectively compensate for the ineffective light trapping of the textured surface of mc-Si solar cells, which is of practically significant for the photovoltaic solar cell industry.

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