

Solar cell performance improvement via photoluminescence conversion of Si nanoparticles

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Photoluminescence (PL) conversion of Si nanoparticles by absorbing ultraviolet (UV) lights and emitting visible ones has been used to improve the efficiency of crystalline Si solar cells. Si nanoparticle thin films are prepared by pulverizing porous Si in ethanol and then mixing the suspension with a SiO₂ sol-gel (SOG). This SOG is spin-deposited onto the surface of the Si solar cells and dries in air. The short-circuit current as a function of Si nanoparticle concentration is investigated under UV illumination. The maximal increase is found at a Si concentration of 0.1 mg/mL. At such concentration and under the irradiation of an AM0 solar simulator, the photoelectric conversion efficiency of the crystalline Si solar cell is relatively increased by 2.16% because of the PL conversion.

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The use of solar cells as electric power supply is one of the solutions to the problems of increasing global energy consumption and decreasing fossil fuel storage^[1]. Moreover, it is almost the only energy source for satellites, space stations, and other outer space exploration activities^[2]. Currently, commercial solar cells normally utilize a narrow band of solar emission spectrum, i.e., from visible to near-infrared regimes, because of the bandgap limitations of the related semiconductors, such as Si, GaAs, CdTe, and CuIn_{1-x}Ga_xSe₂^[3,4]. Thus, the main approach in improving the performance of the current solar cells is the use of upconversion films to convert infrared lights into visible ones and thus increase the absorbed light flux of a solar cell^[3-6]. However, the upconversion probability is so low that its practical application is still currently unavailable. Another approach is the use of downconversion and photoluminescence (PL) conversion mechanisms to convert ultraviolet (UV) lights into visible ones for the same purpose^[3-12]. Although the quantum efficiency of downconversion for current materials could be high, the wavelength range of UV light to be down-converted is usually from 100 to 200 nm, which is hardly covered by the solar spectrum. The PL conversion probability can be on the order of 10%^[3,13,14] compared with that of upconversion, which is less than 0.1%. Thus, PL conversion is practically and technically important particularly for solar cells used in the outer space and highlands because the amount of UV light (~ 250 nm $< \lambda < 390$ nm) from the sun is relatively high^[9-12]. During the investigation of Si nanoparticle light emissions, Si nanoparticles were found to absorb UV light and emit red or near-infrared ones^[9-14]. This feature of PL conversion can be used to improve the performance of crystalline Si solar cells^[9-12], particularly the dominant ones in the market today, which absorb red light most efficiently. In this letter, the correlation between the PL emissions of Si nanoparticles dispersed in SiO₂ and the short-circuit current of crystalline Si solar cells was first studied under UV light illumination. Then, the response

of Si solar cells coated with SiO₂ thin films containing Si nanoparticles was studied under the illumination of an AM0 solar simulator that mimics the solar emission spectrum in outer space.

A porous Si sample was prepared via standard electrochemical etching of Si wafer (p-type (100) with resistivity of 0.01 Ω -cm) in an etching solution consisting of hydrofluoric (HF) acid, ethanol, and H₂O₂ at a volume ratio of 13:27:1.6, respectively. The concentrations for the as-received HF acid, ethanol, and H₂O₂ were 40%, 99.9%, and 30%, respectively. The current density was maintained at 35 mA/cm² during etching to obtain a thick and homogeneous porous Si layer. The as-prepared porous Si sample was then dipped in H₂O₂ for 5 min for surface oxidation. Thereafter, a bright reddish luminescence under UV excitation was observed. The porous Si sample was pulverized in ethanol in an ultrasonic bath to obtain a silicon nanoparticle suspension, which was then mixed with a SiO₂ sol-gel (SOG) or SOG-700A (Spintronics, Ltd., New Zealand). Various concentrations of Si nanoparticles in SOG were prepared by adjusting the proportion of Si nanoparticle suspension, ethanol, and SOG. The concentrations of SOG in different colloidal solutions remained constant. Finally, the SOG containing Si nanoparticles was spin-deposited on the crystalline Si solar cell as the PL conversion film. All measurements were conducted after the SOG solidified at room temperature for 3 h. The SOG thickness was ~ 150 nm, and the size of the Si nanoparticles was within 3 to 5 nm, as estimated from the PL position. The crystalline Si solar cells were offered by the Shanghai Institute of Space Power Supply. The surface size of the solar cells was 20 \times 15 (mm). Moreover, a P-type single-crystalline Si wafer with a thickness of 0.2 mm was used as substrate, and the PN junction was made after doping at the surface region. No anti-reflecting thin film such as Si₃N₄ was grown, and the cell surface was not textured. Both the back and front grid electrodes were made of Ag. The height of the Ag grid on the front surface was 3 μ m.

The reflectance, absorption, and transmittance spectra

of the PL conversion film were measured using a UV-visible near-infrared spectrophotometer (UV-3101PC, Shimadzu, Japan). The PL spectrum was measured using a fluorescence spectrometer (F4500, Hitachi, Japan). For the optical measurements, the SOG containing Si nanoparticles was spin-deposited on a quartz or Si substrate. A He–Cd laser was used as the UV source ($\lambda = 325$ nm) to examine the response of the Si solar cells in the UV regime. An AM0 solar simulator system (X-25, Spectrolab, USA), which mimics the solar illumination in outer space, was used to measure the $I - V$ property of the solar cells after PL conversion. The external quantum efficiency (EQE) of the solar cells with or without PL conversion film was measured using an IQE-200TM system (Newport/Oriel).

Although the measured $I - V$ curves of the as-received solar cells are almost the same, to ensure precise comparability of the different PL conversion processes, the I values of the as-received cells were slightly adjusted by multiplying them with numbers very close to 1, so that all the $I - V$ curves of the as-received cells would be exactly the same as that of a selected “standard cell.” Then, after different cell treatments, the measured $I - V$ curves were corrected in the same manner as that before treatment. Doing so removed errors due to cell differences.

Figure 1 shows the absorption and PL spectra of the Si nanoparticles from a suspension of Si nanoparticles at a concentration (C_{Si}) of 0.05 mg/mL. The absorption edge was approximately <350 nm in the UV regime, whereas the PL emission peaks were at 645 nm, falling within the wavelength range mostly favored by crystalline Si solar cells. The result demonstrates the PL conversion from the UV light to red ones by Si nanoparticles. Figure 2 shows the plot of the increase in the short-circuit current I_{SC} of crystalline Si solar cells coated with SOG containing Si nanoparticles with respect to that of bare Si solar cells as a function of C_{Si} . During the I_{SC} measurement, the UV light beam was normally incident toward the cell surface with a beam size of $\phi = 1.0$ cm after beam expansion. The PL intensity, measured as the peak height versus C_{Si} , was also depicted. As the C_{Si} in the SOG increased, the PL intensity steadily increased. However, the I_{SC} initially increased and then dropped after reaching the maximum of 38% at a C_{Si} of 0.1 mg/mL. The measured EQE was 9.4% at a C_{Si} of 0.1 mg/mL with $\lambda = 325$ nm, whereas that at a C_{Si} of 0 mg/mL (SOG without Si nanoparticles) was 8.6%. The EQE for the

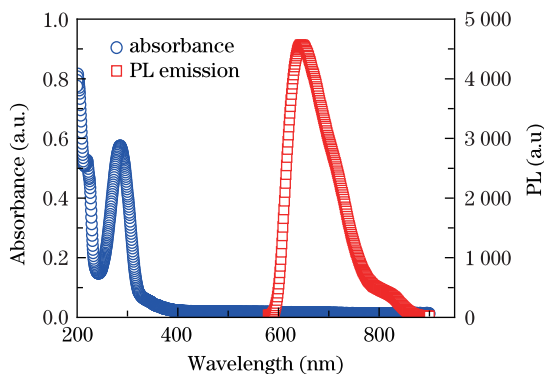


Fig. 1. Absorption and PL spectra of Si nanoparticles.

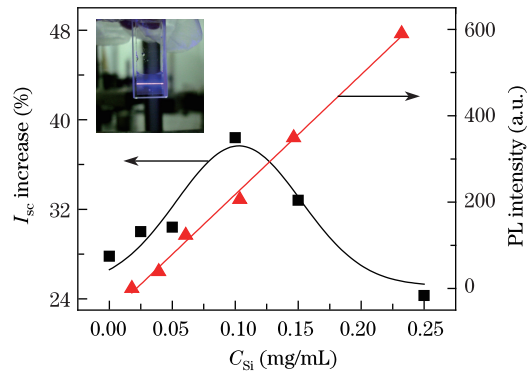


Fig. 2. Relative increase of short-circuit current and PL intensity versus Si nanoparticle concentration under UV illumination.

bare solar cell was 6.6%. Hence, compared with the bare solar cell, the relative increase in EQE at a C_{Si} of 0.1 mg/mL with $\lambda = 325$ nm is 42.4% and that for pure SOG is 30.3%. These relative increases in EQE generally agree with those of I_{SC} , i.e., 38% and 28%, respectively, as shown in Fig. 2. The inset of Fig. 2 shows a suspension of Si nanocrystals in ethanol at a C_{Si} of 0.1 mg/mL in a quartz container. Due to the PL conversion, a He–Cd laser beam ($\lambda = 325$ nm) shone through, and a bright red line could be clearly seen by the naked eye. The increase in I_{SC} again demonstrated the validity of PL conversion in increasing the I_{SC} of crystalline Si solar cells^[8,11]. However, the open-circuit voltage, U_{OC} , was nearly constant with the change in C_{Si} . Two factors affect the change in I_{SC} with increasing C_{Si} , namely, the increasing PL conversion that is good for increasing I_{SC} , and the increasing scattering of UV lights and visible ones, which tends to minimize I_{SC} . Therefore, a compromise of C_{Si} for I_{SC} between these two factors exists. A concentration of 0.1 mg/mL was selected for further experimentation under AM0 illumination.

The $I - V$ curve of the crystalline Si solar cell covered by a SOG thin film containing Si nanoparticles at a C_{Si} of 0.1 mg/mL (named “SOG+Si-np”) was measured using an AM0 solar simulator system. For comparison, the $I - V$ curves of the solar cell coated with pure SOG of the same thickness (named “SOG”) and of the bare solar cell (named “bare”) were also recorded. These curves are shown in Fig. 3. The measured parameters of I_{SC} , U_{OC} , fill factor (FF), and photoelectric conversion efficiency η for the three samples are listed in Table 1. The areas surrounded by the $I - V$ curves of SOG and SOG+Si-np were considerably greater than that of bare, suggesting their much greater efficiencies, as shown in Table 1. The reflectivity of light was decreased after the solar cell was coated with the SOG film as the light impinging on the SOG-coated sample experienced a relatively slow variation in refractive index^[15]. Hence, the light flux collected by the solar cell was increased. On the other hand, with regard to the difference between the $I - V$ curves of SOG and SOG+Si-np, although the change in the $I - V$ area was not very significant, the area surrounded by the $I - V$ curve of SOG+Si-np was still larger than that of SOG. This finding is more evident in the enlarged part shown in the inset of Fig. 3. As shown in Table 1, η increases from 12.95% to 13.23% or η relatively increases

by 2.16%. From Fig. 3, even considering the change in FF, as listed in Table 1, the increase in η is still clear. An optimized C_{Si} was selected. Thus, the increase in η due to PL conversion is evidently greater than those previously reported^[3,9].

The reflectance spectra for the SOG and SOG+Si-np were measured, as shown in Fig. 4, to prove that the increase of η is truly due to PL conversion. The substrates were Si. The difference between the reflectance values of these two samples is small. In fact, the reflectance of SOG+Si-np at the wavelength of $\lambda=600$ to 800 nm, the most favorable light regime for crystalline Si solar cells, is even slightly greater than that of SOG. Hence, if PL conversion did not occur, the measured η of SOG+Si-np would be less than that of SOG, in contrast to the results in Fig. 3 and Table 1.

In conclusion, this letter shows the validity of PL conversion in improving the efficiency of crystalline solar cells. The PL conversion film in the current study adopts a SOG containing Si nanoparticles. These nanoparticles are prepared by pulverizing porous Si in ethanol and then mixing the suspension with SOG at desired

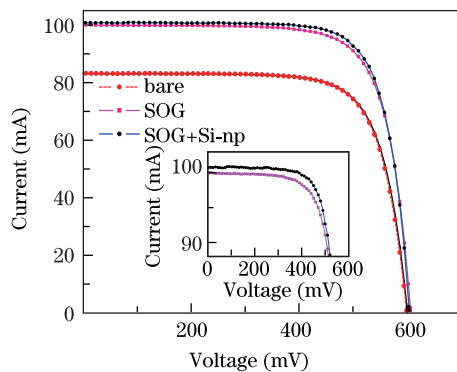


Fig. 3. $I - V$ curves for bare Si solar cell, Si solar cell coated with SOG, and Si solar cell coated with SOG containing Si nanoparticles. The curves were measured under AM0 simulator illumination. The inset shows an enlarged part of the $I - V$ curves of SOG and SOG+Si-np.

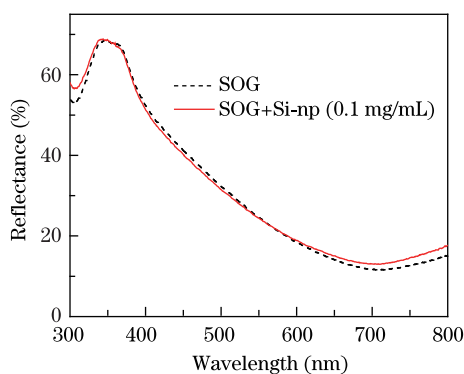


Fig. 4. Reflectance spectra for the SOG thin films with and without Si nanoparticles.

Table 1. Parameters for Different Si Solar Cells

Sample	I_{SC} (mA)	U_{OC} (V)	FF	η (%)
Bare	83.1	0.601	0.748	10.61
SOG	100.0	0.607	0.751	12.95
SOG+Si-np	100.7	0.606	0.763	13.23

concentration ratios. The current study shows that PL conversion increases the photoelectric conversion efficiency of crystalline Si solar cells by 2.16% in an AM0 environment. Compared with those of similar works, such as those using rare-earth materials for PL conversion^[16], the emission spectrum of Si-np has a broader wavelength range, which is beneficial for visible-light applications.

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