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Effective light trapping by hybrid nanostructure for crystalline silicon solar cells



Solar Energy Material

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ABSTRACT

Ag nanoparticles (NPs), as etching catalyst, are applied onto the pyramid textured surface of the semifinished single crystalline silicon solar cell by spraying a solution containing AgNO₃ and sodium citrate. Upon chemical etching, nanopits are formed with the Ag NPs staying inside of the nanopits. Complete solar cells with and without the Ag-assisted etching are fabricated to study the effects of the hybrid nanostructure. It is found that the optical reflection is effectively reduced by the nanostructure and the incident light is harvested more effectively for enhanced external quantum efficiency (EQE) by as much as 17% for the cells before the SiNx anti-reflection coating, and the EQE can be further enhanced by applying an electric bias 1 V during the EQE measurement. It is believed that when the solar cell with the Ag NPs is illuminated, the local surface plasmon resonance (LSPR) is induced at the specific wavelength regions around 405 and 810 nm. For ultraviolet light, the LSPR effect dominates the increases of the EQE while the effective medium effect is also believed to be responsible for the effective light trapping.

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1. Introduction

Among various semiconductor materials, silicon is the material of choice for photovoltaic (PV) applications due to its low cost, abundance on earth, non-toxicity, long-term stability, and well-established technology. The silicon based solar cells account for 90% in overall PV installations. As one of the primary costs for silicon photovoltaic cells stems from the materials consumption, e.g., Si wafer alone represents almost a half of the module costs [1–3]. The most effective cost-cutting measure is by increasing solar cell efficiency. Light trapping by confining the light within the active semiconductor layers to promote the absorption, may accomplish both efficiency improvement and cost cutting, it is therefore a favorable and effective strategy. Nanoparticles and nanostructures have been successfully used for the light-trapping applications [4,5]. In fact, a facile method using metal-assisted chemical etching has been developed to prepare large-area silicon nanostructure based on metal-catalyzed site-specific anisotropic Si etching mechanism [6-9]. It is simple, low-cost, and large-area compatible for generating Si nanostructures, including nanowires, nanoholes and nanopillars [6,7,9-11].

A few novel methods have been proposed to enhance the light trapping effect. For example, the introduction of local surface

http://dx.doi.org/10.1016/j.solmat.2015.04.019 0927-0248/© 2015 Elsevier B.V. All rights reserved. plasmon resonance (LSPR) effect induced by metallic nanostructures has been widely recognized to be able to boost the light absorption of solar cells. The LSPR effect of noble metal nanoparticles (NPs) has attracted considerable attention in PV research due to its special characteristics: when the metallic NPs are excited by light at specific wavelengths, the collective movement of conduction electrons builds up polarization charges on the particle surface. The key phenomena lie in two main aspects. Firstly, the LSPR can excite electron-hole pairs or increase the rate of electronhole formation in the semiconductor by transferring the plasmonic energy from the metal to the semiconductor [12–15]. Secondly, the LSPR boosts the light absorption of solar cells due to the far-field scattering from the metal NPs [16,17]. Both the shape and size of the metal nanoparticles are found to be key factors in coupling between the metal particles and the dielectric, and thereby the overall enhancement in the optical absorption efficiency [18-21]. The LSPR effect is currently being exploited in various applications including molecular sensing [22-24], light focusing [25], near-field optical microscopy [26], and subwavelength photonics [27]. Various metal nanoparticles are found to support the LSPR effect. In particular, Ag, Au, Cu, and Al nanoparticles have been explored to enhance the solar cell efficiency [28–32].

In this work, we found that a hybrid nanostructure that combines advantages of nanopits and Ag NPs effectively enhances the light absorption and thereby quantum efficiency (QE) of the solar cells. The Ag NPs were prepared as the catalyst to etch the surface

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of single crystalline silicon surface, resulting in a hybrid nanostructure including silicon nanopits and Ag NPs within the nanopits. It is found that the solar cells with the hybrid nanostructure have significantly enhanced short-circuit current density (J_{SC}) by 17%. At the same time, the QE response clearly supports the interpretation that the increased current is from the LSPR effect.

2. Experimental

Semi-finished single crystalline silicon solar cells, acquired from a production line after the alkali anisotropic etching but prior to the SiNx anti-reflection (AR) coating, are used for this study. The Ag NPs were prepared by reducing AgNO₃ (0.01 M) using sodium citrate $(7 \times 10^{-3} \text{ M})$ at about 100 °C. To apply the Ag NPs onto the silicon solar cell surface in a well-controlled fashion, a single crystalline silicon solar cell was heated to slightly above 100 °C first, the preformed Ag NPs colloid suspension was then spraydeposited onto the preheated solar cell surface using a pressure regulated air brush spray system. As the water solvent evaporates as it reaches the solar cell surface maintained at above 100 °C, the Ag NPs are "fixed" onto the cell surface. A chemical etching process, using DI water-HF-H₂O₂ (volume ratio=30:4:1, C_{HF}=40%, $C_{H_2O_2} = 30\%$), was used to form silicon nanopits on the wafer surface with a diameter about 30 nm on the pyramid structure. The Ag NPs can be easily removed by reacting with nitric acid for 30 min. Both the sample surface and its cross-section were examined using a scanning electron microscope (SEM, S4800, HITACHI). A Kratos Axis Ultra-XPS system was used with a monochromatic Al-Ka source. The AR properties of structured samples were measured by using a QE measurement system (QTEST STATION 500TI, CROWNTECH) equipped with integrating sphere. The QE measurement system was also used to record incident photon current conversion efficiency spectra before and after the chemical etching.

3. Results and discussion

It is known that the Ag NPs in colloid suspension exhibit characteristic peaks in the UV-vis absorption spectrum. Fig. 1 (a) shows the UV-vis absorption spectra of Ag NPs prepared with different diameters at 25, 35, 45, and 60 nm. It is clear that the Ag NPs show distinguished LSPR peaks at 404, 412, 425, and 433 nm. Particularly, the Ag NP diameter has a well-established relationship with its LSPR peak position. Fig. 1(b) shows XPS of Ag NPs deposited on the silicon wafer, with two peaks at 368 eV and 374 eV attributed to atomic Ag. Fig. 1(c) shows a SEM image of the 25 nm Ag NPs deposited on a silicon wafer surface, and the measurement is consistent with what calculated from the UV-vis [33,34]. Fig. 1(d) shows the SEM image of the cross-section of the Si substrates after etching. It is obvious that in addition to an array of pyramidal structures about several micrometers, there are smaller nanopits with an average diameter \sim 30 nm on each pyramid. Changing chemical etching time from 1 to 12 min does not alter surface morphology. In order to observe the depth of nanopits, the same method was employed onto the planar single crystalline silicon. Careful observation shows that longer etching time resulted in deeper pits (Fig. 2). When the sample was etched for 1 min, the nanopits were not as obvious. However, increasing the chemical etching time to 3 min, 5 min, 10 min, and 12 min,



Fig. 1. (a) UV-vis absorption spectra of Ag NPs in colloid suspension with different sizes. (b) XPS of the Ag NPs. (c) SEM image of the Ag NPs on Si substrate. (d) Crosssectional SEM image of the solar cell after etching.

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