Fabrication of an ant-nest nanostructure in polycrystalline silicon thin films for solar cells

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A silicon nanostructure is fabricated in polycrystalline silicon thin films by metal-assisted wet chemical etching using thermally annealed silver nanoparticles as a catalyst. The Si nanostructure has an ant-nest feature. Solar cells based on the silicon nanostructure gives 90% short-circuit current enhancement compared to the cells based on the planar film. We also report that Al_2O_3 passivation of the silicon nanostructure provides a new approach to improving the polycrystalline silicon thin film's electrical property. The open-circuit voltage of the Al_2O_3 passivated cells is improved by 70 mV.

Polycrystalline silicon (poly-Si) obtained by solid-phase crystallization of amorphous Si thin films at relatively low temperature (600 °C) is commonly used in the field of large-area thin-film transistors [1]. Solar cells based on this material combine the advantages of standard Si wafer-based technology with low material usage and large-area monolithic construction for thin films [2]. However, solid-phase crystallized poly-Si contains a high density of intragrain defects, which make achieving satisfactory device performance challenging [3,4]. To reduce the number of defects, rapid thermal annealing (RTA) and hydrogen passivation have been developed [5]. RTA uses high temperature, which is limited by the thermal property of the substrate, to eliminate the intragrain defects. Hydrogenation introduces H atoms to deactivate the Si dangling bonds in the poly-Si material. The other challenge for poly-Si thin-film solar cells is light confinement due to poor light absorption of the micron-thick Si film. Various light-trapping methods have been developed, including substrate texturing [6], back surface reflection [7], Si surface texturing [8] and plasmonics nanoparticles [9]. Si nanowire cells showing strong light trapping are fabricated by institute of photonic technology using a wet electroless chemical etching method [10]. The disadvantage of the Si nanowire array structure is its inferior mechanical robustness.

In this contribution, we present the fabrication of an Si nanostructure that can not only improve the poly-Si thin film's optical property, but also the electrical property when passivated by atomic-layer-deposited Al_2O_3. The Si nanostructure is fabricated by metal-assisted wet chemical etching [11] using thermally evaporated Ag nanoparticles. Due to the anisotropic metal-assisted chemical etching and the random orientation of the grains [12] in the poly-Si film, the Si nanostructure has an ant-nest feature, which makes it different from the Si nanohole structure in crystalline Si [13]. A 90% short-circuit current (J_{sc}) enhancement has been achieved due to the improved light trapping and film quality. Atomic layer deposition (ALD) has been developed for years to passivate the surface of Si wafer solar cells [14]. It has not been applied to poly-Si thin film solar cells as the back surface recombination plays a negligible role in such cells [15]. However, we demonstrate in this paper that, by fabricating the Si nanostructure and passivating it using ALD-deposited Al_2O_3, the poly-Si diode's V_{oc} (open-circuit voltage) can be improved by 70 mV. It thus provides a new approach to improving the electrical property of solid-phase crystallized poly-Si thin films besides RTA and hydrogenation.

Two kinds of poly-Si films were prepared: a 3.5 μm thick n-type film for demonstration of J_{sc} enhancement and a 2 μm thick p-type film for demonstration of V_{oc} improvement. The 3.5 μm thick a-Si precursor diode with a *glass/SiN/p⁺/n⁻* structure was deposited by electron-beam evaporation onto planar borosilicate glass with silicon nitride antireflection layer [16]. The absorber was n-type phosphorus doped at 2×10^{16} cm^{-3}. After deposition, the film was crystallized and annealed. Then 14 nm thick Ag film was thermally evaporated onto half of the Si film surface, and was annealed at 230 °C for 53 min in an N_2 atmosphere to form Ag nanoparticles. The poly-Si film half-coated with

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Ag nanoparticles was immersed in an aqueous solution of HF (49%)–H_2O_2 (35%)–H_2O at a volume ratio of 25/10/75 for 3 min. The etching time was controlled so that the etching did not penetrate into the junction. As the etching rate was ~1 μm [17] and the emitter in such kind of cells is about 0.5 μm thick, the etching time was determined to be 3 min. Any residual silver was subsequently removed by diluted nitric acid (69% HNO_3:H_2O, 1:1). The half-etched Si film was cleaned by standard RCA treatment, spin-coated with a phosphorus diffusion source (2% H_3PO_4) and baked at 250 °C for 10 min in air. Subsequently the sample was thermally annealed at 845 °C for 1 min to form a back surface field (BSF) [18]. The sample was then cleaned by dipping in diluted HF and hydrogen plasma passivated. The poly-Si diode was finally metallized to 2 cm^2 cells using interdigitated line contacts on both the emitter and the BSF layers [16]. The 2 μm thick p-type film with a $glass/SiN/n^+/p^-/p^+$ structure was prepared by plasma-enhanced chemical vapor deposition, crystallized, annealed and hydrogen passivated. The p-type film was half-etched for 2 min, then cleaned with RCA, dipped in diluted HF and loaded into the ALD chamber for Al_2O_3 growth at 200 °C.

Scanning electron microscopic (SEM) imaging and transmission electron microscopic (TEM) imaging were performed to characterize the Si nanostructure. Optical spectroscopy was used to characterize the film's reflectance and transmittance. Suns-V_{oc} [19] and external quantum efficiency (EQE) measurements were performed to characterize the cell.

Figure 1(a) shows the Ag nanoparticles on the poly-Si thin film surface. The nanoparticle size is in the order of 150–250 nm with surface coverage of 35%, as calculated by image statistical analysis. In a typical metal-assisted chemical etching procedure, the Si beneath the noble metal is etched much faster than the Si without noble metal cov-erage. As a result, the noble metal sinks into the Si substrate. Pores with opening sizes similar to that of the Ag nanoparticles are clearly seen after 1 min etching in Figure 1(b). They are randomly tilted as the etching proceeds along the crystallographically preferred (1 0 0) direction [17]. When the etching reaches 3 min, nanoholes appear (see Fig. 1(c)) due to the wet chemical etching, which preferentially attacks the defective regions in the film. The inlet SEM image focuses on a single pore. Nanometer-sized holes are observed in the sidewall of the pore. Figure 1(d) shows the cross-section of the etched region under SEM depicting the ant-nest feature of the Si nanostructure. The cross-section TEM image in Figure 1(e) clearly shows the Ag nanoparticles' penetrating path in two adjoining grains, especially the one starting from the right-hand side grain that changes its direction at the grain boundary.

To obtain more information on the nanoholes, a TEM image of a single grain in a dark field was taken and compared with that in a bright field, as shown in Figure 2. The TEM image in the bright field shows the presence of the nanoholes in the etched region. In the dark-field TEM image, the intragrain defects (mainly dislocations) are revealed as bright lines. By comparison, it can be seen that fewer dislocations are present in the etched region, indicating that the nanoholes are etched defective locations in the grains. Intragrain defects are known to be the limiting defects in poly-Si thin films [3,20]. While the grain boundaries can be passivated well by hydrogenation, hardly any intragrain defects are eliminated after RTA and hydrogenation. The result in this work shows that the intragrain defects can be etched and turned into surface recombination sites, which makes new treatment on the defective poly-Si films possible.

The EQE (left axis) measured on the cell fabricated on the Si nanostructure from the glass side is compared with the planar reference cell in Figure 3(a). Also shown is the
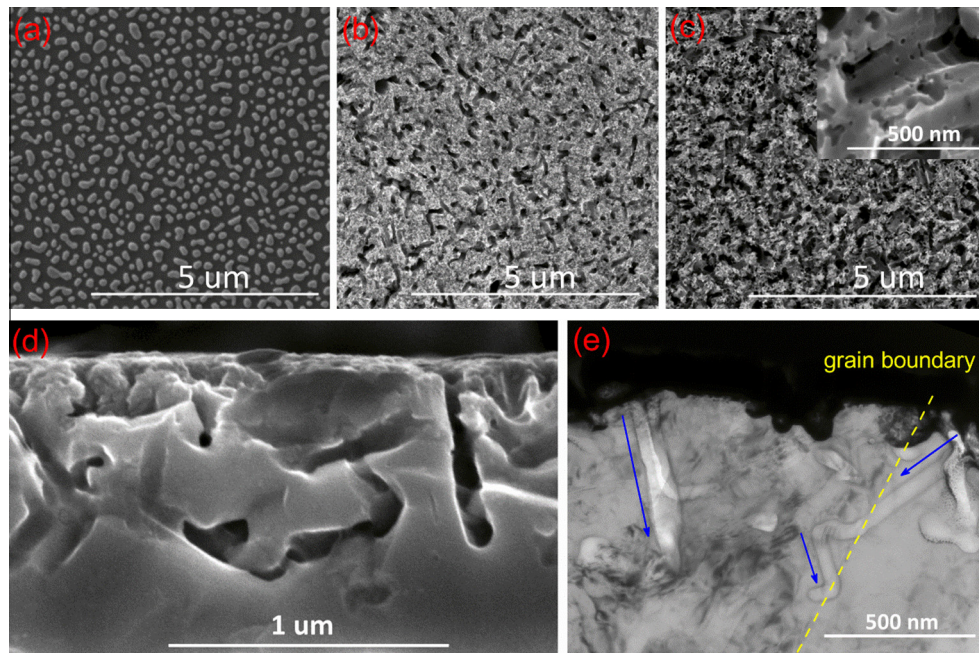

Figure 1. (a) Ag nanoparticles on the poly-Si film surface; (b) the film surface after 1 min etching in HF/H_2O_2/H_2O solution; (c) the film surface after 3 min etching in HF/H_2O_2/H_2O solution; (d) cross-section of the etched region showing an ant-nest feature; (e) TEM image showing the Ag nanoparticle penetrating path in two adjoining grains (as directed by the blue arrows). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)