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Fabrication of inverted pyramid structure by Cesium Chloride self-assembly lithography for silicon solar cell

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ABSTRACT

Inverted pyramids were fabricated through a method combining cesium chloride (CsCl) self-assembly technology and anisotropy corrosion of silicon solar cells. Ti film with nanoporous masks was formed by lift-off the CsCl nanoislands for the inverted pyramids. The pyramids were then formed by anisotropy corrosion of alkaline solution. The average diameter and morphology of the pyramids were controlled by varying the average diameter of CsCl nanoislands from 400 nm to 1.5 μm and by varying the etching time of alkaline solution from 2 to 8 min. The inverted-pyramid texture could suppress reflection to below 10% at wavelengths from 400 to 1000 nm, which was much lower than that of planar wafer. A solar cell fabricated from the pyramids had higher short-circuit current density (J_{sc}) and photovoltaic conversion efficiency (PCE) compared with those of planar solar cells for the good antireflection property. The solar cell showed a PCE of 15.25%, a J_{sc} of 38.35 mA/cm^2, and an open-circuit voltage of 555.7 mV.

1. Introduction

To prepare high-efficiency monocrystalline silicon (c-Si) solar cells, the surface reflection of light should be minimized. Formation of Si with pyramidal structure decreases surface reflection substantially. Such structure includes random traditional pyramids and inverted pyramids. Compared with traditional pyramids, inverted pyramids are more efficient with single-sided geometric light trapping because they have superior internal response, increased path length, and reduced front-surface reflectance, which can improve the short-circuit current of solar cells [1,2]. Both pyramids are easily obtained by anisotropy corrosion of silicon using alkaline solutions such as those of NaOH [3], KOH [4], Na_2CO_3[5], and Na_3PO_4[6]. The side length of the rectangular base of traditional pyramid structures are usually 4–8 μm, and their etching time in alkaline solution is >20 min [7,8]. Inverted-pyramid textures with low reflectance have been formed by alkaline etching with an oxide mask [9,10]. UV lithography is often used in the formation of etching masks. In UV lithography and etching, a pattern is formed on the Si surface through application of the resist, exposure, development, and etching. Numerous processes increase the production cost. The diameter of the pyramids, as determined by UV lithography, technology, is >1 μm. Recently, laser-based techniques have been proposed. In these techniques, a laser-patterned hard layer such as SiO_2 or SiN_x is used as the etching mask for anisotropy corrosion [11,12]. The mask film is directly patterned by laser ablation, but this method is costly. With the development of nanotechnology, silicon nanostructures have received much interest because of their potential application in solar cells. Nanoscale inverted pyramids have also attracted much attention. The surface morphology of silicon nanostructure enable it to absorb more light [13–16].

Cesium chloride (CsCl) self-assembly is a method that uses nanoisland/dot fabrication. The method, which is based on the deliquescence of salt, was invented by Mino in the last decade [17]. On exposure to water vapor, some CsCl dissolves in the layer of absorbed water on the CsCl film, and variations in its local concentration increase with increasing surface curvature. Lateral concentration gradients of CsCl in the continuous surface cause smaller grains to disappear by completely dissolution in the absorbed water and cause the film to become more discontinuous, leading to rapid island formation. The system of CsCl nanoislands changes with time to decrease its overall surface-to-volume ratio, since the surface constitutes a region of excess energy [17,18].

In this paper, we fabricated nanoscale inverted pyramid structures for silicon solar cells by CsCl self-assembly and anisotropy corrosion. The nanoislands were originally fabricated through CsCl self-assembly method, which allows evaporation of the thermal coating, facile formation involving water, and removal using water

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[18–21]. Titanium (Ti) template as etching masks against the anisotropy corrosion was formed by lift-off CsCl nanoislands. After 2–8 min anisotropy corrosion in alkaline solution, inverted pyramid structures with 400 nm to 1.5 μm average diameter covered the entire silicon surface. With this inverted-pyramid surface texture, the reflectivity was reduced to $<10\%$. The efficiency of the solar cell with this inverted pyramid surface texture was ~15.25%, which is much higher than that of the planar solar cell with good light trapping property fabricated through the same process.

2. Experimental

Fabrication of the inverted pyramid structures was carried out on polished (100) *p*-type c-Si wafers (1–3 Ω cm resistivity, 2 in and 350 μm thickness). Before etching, the Si wafer was cleaned with piranha solution (H_2SO_4:H_2O_2 at 3:1 ratio by volume, 80 °C, 60 min). In the first step of the process (Fig. 1a), CsCl film with a certain thickness was deposited by heat evaporation onto the wafer surface in the high-vacuum system (0.01 Pa). The thickness of the CsCl film was monitored by a thickness monitor during the entire evaporation process. The deposition speed was ~1 nm/s, and the thickness of CsCl film, which decided the average diameter of the nanoislands, was hundreds of nanometers. When the heater cooled down and the mechanical pump stopped, the vacuum chamber was filled with gas with relative humidity of 40–75%. The CsCl on the substrate grew, forming CsCl nanoisland arrays by absorbing water in the air during the development process (Fig. 1b). The CsCl film could develop nanoislands at a relative humidity and developing time compatible to the CsCl film thickness. Details of the developing conditions are listed in Table 1 [19]. Ti film of 40 nm thickness was deposited onto the substrate by thermal evaporation using a 99.99% pure Ti source, and the Ti-coated structure was subsequently agitated by ultrasonication in deionized (DI) water for 2 min. This resulted in complete removal, i.e., lift-off, of the Ti-coated CsCl nanoislands, leaving a Ti coating with a nanoporous silicon surface (Fig. 1c and d). The wafer surface was then coated with the inverted pyramid structures and rinsed thoroughly with NaOH (1.5 wt%) solution, $Na_2SiO_3 \cdot 9H_2O$ (1.5 wt%) solution, IPA (6.5%), and DI water (90.5%) at 80 °C for 2–8 min (Fig. 1e). Finally, HF (5%) and DI water were used to remove the Ti masks to expose the inverted pyramid structures (Fig. 1f).

After surface texturization, the wafers were subjected to phosphorous diffusion using $POCl_3$ at 850 °C for 13 min. The back and circumferential junctions were then removed by inductively coupled plasma (ICP) dry etching with the following etching conditions: 5 min etching time, 150:10 sccm SF_6/He gas ratio, 600 W excitation power, 50 W bias power, and 4.5 Pa chamber pressure. About more than 1 μm thickness of silicon was removed. A thin Al layer was deposited on the rear surface by thermal evaporation and alloying in ambient N_2 at 700 °C to form a back-surface field. Finally, the front metal contact was prepared by Ti/Ag (40:1000 nm) deposition through metal masks followed by annealing at 400 °C for 2.5 min in ambient N_2. All cells were cut into $1 \times 1\ cm^2$ pieces for testing.

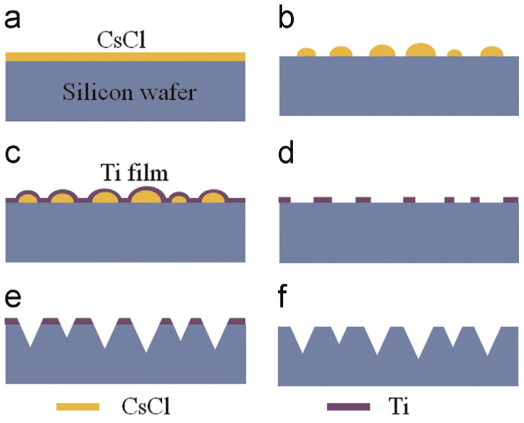

Fig. 1. .

Table 1
Developing conditions to form nanoislands of different average diameters.

Average diameter (nm)	Film thickness (nm)	Relative humidity (%)	Developing time (min)
400	200	40	30
700	350	50	50
1000	500	60	60
1500	750	75	90

CsCl film was deposited by using a vacuum-coating machine (DM-300B) with thickness monitor (Maxtek, inc. TM-200). The back and circumferential junctions were etched by an ICP etcher (ICP-98A, Institute of Microelectronics, Chinese Academy of Sciences). The morphologies of the nanostructures were examined by scanning electron microscopy (Hitachi-S4800). Optical reflectance spectra were obtained at normal incidence of light by using a UV–visible near-infrared spectrophotometer (Hitachi UV-4100). Bright *J–V*curves were obtained under a full-spectrum solar simulator at AM 1.5 (1000 W/m^2 at 25 °C, Oriel).

3. Results and discussion

3.1. Morphology of the inverted pyramid structures

Fig. 2a shows the morphology of the substrate with CsCl nanoislands of 400 nm average diameter formed by self-assembly. After Ti deposition and ultrasonic agitation in DI water, a nanoporous Ti coating with 400 nm average diameter remained on the silicon surface (Fig. 2b). The planar silicon surface without Ti protection was anisotropically etched with the alkaline solution to form numerous inverted pyramid structures on the silicon surface. After 2 min of anisotropic etching, the pyramids had ~500 nm width and 250 nm depth, as shown in Fig. 2d.

The average diameter of the inverted pyramid structures were controlled by the average diameter of the nanoporous Ti film formed by CsCl lift-off and by the anisotropic etching time of the alkaline solution. The CsCl nanoislands on the polished surface had average diameters of 50 nm to 1.5 μm [19]. However, nanoislands were difficult to lift off from the nanoporous Ti film. Therefore, nanoislands with average diameters ranging from 400 nm to 1.5 μm formed on the Ti film.

Anisotropic etching occurred because the etching rate of silicon in the $<111>$ direction was low compared with that in the $<100>$ direction. In the dilute alkaline solutions, the etching rate of $<100>$ silicon was about 0.1–0.5 μm /min, whereas that in the $<111>$ and $<100>$ directions was only $<10\%$, leading to an inverted pyramid morphology [22,23]. The silicon on the nanoporous on Ti film exposed to the alkaline solutions were thus anisotropically etched by the alkaline solution, while the silicon under the Ti film protection remained planar. As the etching time increased, more alkaline solution permeated the Ti film, and the average diameter of the inverted pyramids increased.

Fig. 3 shows the morphology of the substrates with inverted-pyramid texture, which were fabricated by using Ti film with 400 nm average diameter as nanoporous masks. The etching time was increased from 2 to 8 min. When the etching time was 2 min, the average diameter of the inverted pyramids was ~400 nm, and