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Fabrication of silicon nanopillar arrays by cesium chloride self-assembly and wet electrochemical etching for solar cell

Jing Liu[a,b], Xinshuai Zhang[a,b], Gangqiang Dong[b], Yuanxun Liao[c], Bo Wang[a], Tianchong Zhang[a], Futing Yi[a,*]

[a] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] ARC Photovoltaics Centre of Excellence, UNSW, Sydney 2052, Australia

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ABSTRACT

A simple technology with cesium chloride (CsCl) self-assembly lithography and wet electrochemical etching is introduced to fabricate the wafer scale, disordered, well-aligned, and high aspect ratio silicon nanopillars. The original nano structures of CsCl islands with diameters of 500–2000 nm are formed by self-assembly and used as template of lift-off for the nanoporous gold film for wet electrochemical etching as the catalyst in etching solution of HF and H_2O_2. The average diameter of silicon nanopillars is determined by the CsCl nanoislands with 500–2000 nm, and the height of silicon nanopillars is mainly determined by the etching time in etching solution with 3–12 μm. The aspect ratio can achieve to 60. The solar cells with different height nanopillars are made for the research of photovoltaic conversion efficiency (PCE). The reflectance of the nanopillars with different height is measured from the wavelength of 400 to 1000 nm and the 9 μm height silicon nanopillars has the lowest one which is below 3%. The PCE shows the highest value of 14.19% at the condition of 3 μm height nanopillars and 12.18% of planar one with the same fabrication process.

1. Introduction

Silicon nanostructures such as nanowires, nanocones, or nanoporous have been fabricated with the development of nanotechnology [1–3]. Silicon nanopillars based solar cells have attracted great attention recently due to their potential applications for the next generation solar energy conversions because of the unique properties in the fields of antireflection, light trapping, and carriers' radial separation mechanisms [4,5]. Many methods have been employed to fabricate nanopillar structures, such as nanoimprint lithography [6,7], the e-beam and laser interference lithography [8,9], reactive ion etching (RIE) [10–12], metal-assisted electrochemical etching [13–16], and so on. In the case of dry etching, such as RIE, inductively coupled plasma (ICP) dry etching, the silicon nanopillars or nanowires typically have a sidewall angle of ca. 10–20° [17]. Compared with the dry etching, the wet electrochemical etching method is low-cost, and well controlled, which is preferred for the fabrication of high aspect ratio structures [14]. Nanosphere lithography combined with the gold (Au) film assisted electrochemical etching method has been widely used to fabricate periodic high aspect ratio silicon nanopillars [15].

Cesium chloride (CsCl) self-assembly, based on the deliquescence of salt, is a simple method to fabricate disordered CsCl nanoislands, which have successfully been used as nanomasks to make nanopillars, nanoscrews, nanoholes, and some other micro-nano structures through ICP dry etching [18–22]. In this work, we used the CsCl self-assembly nanoislands technology and Au film assisted electrochemical etching method instead of ICP dry etching to finish the fabrication of disordered and high aspect ratio nanopillar arrays. A nanoporous Au template as catalyst during wet etching process to get nanopillars is formed by thermal deposition of Au film on CsCl islands and lift-off in deionized (DI) water. Random distributed nanopillars of 3 μm to 12 μm heights made by this method on the 2 in silicon wafer can suppress the average reflectance below 3% over the range of 400–1000 nm wavelength. The solar cell with nanopillar arrays of 3 μm height and 500 nm average diameter possesses the best solar cell performance with a photovoltaic conversion efficiency (PCE) of 14.19%.

2. Experimental

The overall fabrication process is schematically depicted in Fig. 1. Firstly, after the silicon wafer (p-type, resistivity of 1–3 Ω cm)

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* Corresponding author.
E-mail address: yift@ihep.ac.cn (F. Yi).

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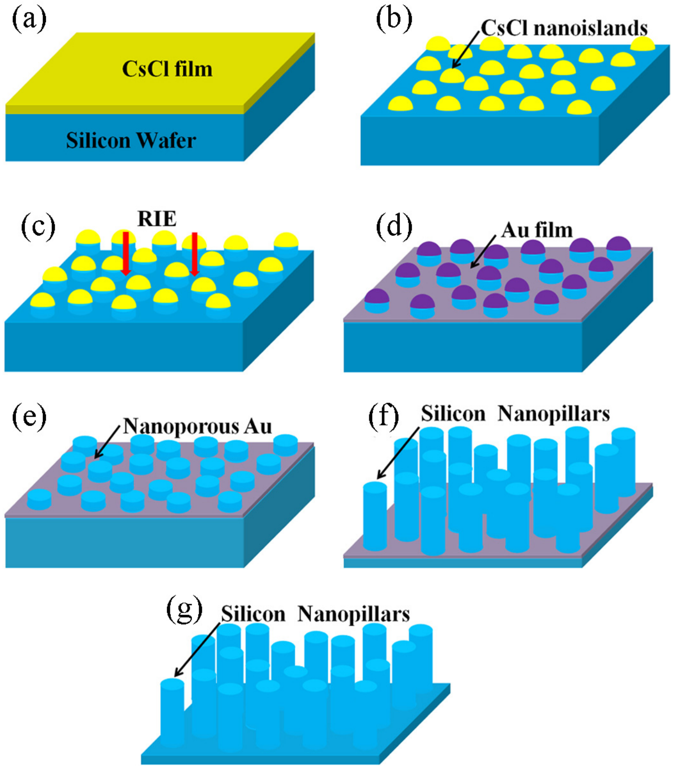

Fig. 1. Fabrication process of the nanopillar structure by CsCl self-assembly lithography and wet electrochemical etching: (a) depositing of CsCl film; (b) development for CsCl nanoislands; (c) RIE for silicon nano steps under CsCl nanoislands; (d) depositing Au film; (e) lift-off for nanoporous Au film; (f) etching of silicon by wet etching and (g) removing nanoporous Au film.

cleaned in H_2O:H_2SO_4:H_2O_2 (5:4:1), a layer of certain thickness CsCl film is deposited by heat evaporation onto the surface of substrate in high vacuum system (0.01 Pa) (Fig. 1a).And under some humidity for development, some CsCl grow up to form nanoislands array on the silicon surface (Fig. 1b). Secondly, RIE dry etching with sulfur hexafluoride (SF_6) under excitation power 60 watt and chamber pressure 5 Pa for 30 s is carried out to etch the silicon, leaving 300 nm depth steps under CsCl nanoislands (Fig. 1c). This morphology can make the Au film to be lifted off on the CsCl nanoislands and form the nanoporous Au film easier. Thirdly, 40 nm thickness Au is deposited onto the substrate by thermal evaporation with a 99.99% pure Au source (Fig. 1d). Then, the Au film is ultrasonically agitated for 2 min to let Au on the CsCl nanoislands be completely removed to form the nanoporous Au film for metal-assisted electrochemical etching (Fig. 1e). Next, for the solution etching process, an etching mixture consisting of deionized (DI) water, hydrofluoric acid (HF), and hydrogen peroxide (H_2O_2) with the concentrations of 4.6 M of HF and 2.2 M of H_2O_2 is used at room temperature to etch the silicon for getting the different depths according to the etching duration from 15 to 60 min (Fig. 1f). During the etching process, bubbles are periodically removed from the surface of samples via gentle agitation in efforts to ensure a homogeneous etching. Finally, the wafer is immersed in gold corrosive liquid (KI: I: DI water = 115 g: 65 g: 100 ml) to remove the nanoporous Au film (Fig. 1 g). The disordered nanopillars with desired heights from 3 μm to 12 μm cover the wafer scale silicon surface by controlling etching time.

The fabrication of silicon solar cells with nanopillars are performed by a conventional solar-cell-fabrication protocol. After surface texturization with nanopillars fabricated by the metal-assisted electrochemical etching, the wafers are subjected to phosphorous diffusion using $POCl_3$ at 850 °C for 13 min followed by back and circumferential junctions removal by RIE. Thin aluminum (Al) layer is deposited on the rear surface by thermal evaporation and alloying in N_2 ambient at 700 °C to form a back-surface field (BSF). Finally, the front metal contact are made by Ti/Ag (40:1000 nm) deposition through metal shadow masks followed by annealing at 400 °C for 2.5 min.

3. Results and discussion

3.1. Morphology of nanopillar structure

Fig. 2 shows scanning electron microscopy (SEM) images of the nano structure at various stages of the nanopillar fabrication process. Fig. 2a is that the CsCl nanoislands with 500 nm average diameter on the silicon surface after development. After RIE, the silicon nano steps about 300 nm height are made under CsCl nanoislands revealed in Fig. 2b. In fact, because of the lattice mismatch between Si and Au, the Au film is difficult to adhere with the planar silicon surface during the lift-off process which leads to the Au film fall off. These nano steps morphology can completely separate the Au film on the CsCl nanoislands from that beside it on the silicon and can easily lift the Au film on it off in DI water with ultrasonically agitation to leave nanoporous Au film on silicon. Fig. 2c shows a 40 nm thickness Au film with holes pattern by the non-closely packed nano steps after lift-off. Fig. 2d is the nanopillars fabricated by 30 mins electrochemical etching and determined in diameter by the holes of Au film. The right one of Fig. 2e shows a photography of a 2 inches silicon wafer with nanopillars of 500 nm average diameter and 6 μm height which has dark surface appearance comparing the planar one in the left of Fig. 2e. During the solar cell fabrication process, the change of the nanopillars morphology is unobvious and the average diameter of nanopillar in the finished cell is slight smaller than the original one because the SiO_2 layer produced in phosphorous diffusion on the surface of nanopillars have been removed.

The average diameter of nanopillars are determined by the Au film holes controlled by the average diameter of CsCl nanoislands which can cover average diameter ranging from 50 nm to 2 μm on a polished surface. However, the nanoporous Au with the holes only from 500 to 2 μm can be fabricated because the small CsCl islands below 500 nm diameter are difficult to be lifted off which results in the absence of the small holes in Au template. Fig. 3a–d show the cross-section SEM images of silicon nanopillars that are created by wet etching for 15, 30, 45, and 60 min, respectively and the corresponding pillar heights are approximately 3, 6, 9, 12 μm. The height of the nanopillars varies linearly with the duration of etching process, with the rate of 200 nm min^{-1}, which provides good control over the height of nanopillar arrays. When the etching time increases to 2.5 h, the nanostructures achieve to over 30 μm height and the aspect ratio is over 60 (Fig. 3f).

3.2. Antireflection property of nanopillar structure

Fig. 4 shows the total reflectance of textured wafers with 3, 6, 9, 12 μm heights nanopillars and planar silicon which are measured by an ultraviolet-visible-near-infrared spectrophotometer (UV-3100) at incidence angle of 8°. From Fig. 4, the nanopillar samples show great antireflection characteristics which depend on the height of nanopillar with the reflectivity of 5% for the 3 μm height nanopillars and 3% for the 9 μm height nanopillars from wavelength of 400 to 1000 nm, while reflectivity of 9 μm height nanopillar wafer is suppressed to below 3% from 400 to 1000 nm wavelength. When the height of nanopillars achieves to 12 μm or more, the reflectivity has no great difference with 9 μm height nanopillar. Obviously, the reflectivity curves also reveal the