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Nanostructured plasmonics silicon solar cells

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ABSTRACT

We report a plasmonics silicon solar cell design, with the possibility of lower cost and higher efficiency. The proposed solar cell consists of a radial p–n junction silicon nanopillar arrays in combination with metallic nanoparticles resolved at the top of the nanopillars. Relatively simple processing methods such as metal assisted electroless chemical etching and spin-on doping techniques are used for the fabrication of the described devices. Prior to the metallic nanoparticle incorporation, the power conversion efficiency of the solar cell with nanopillar arrays with a height of 800 nm was measured to be 10.7%. Subsequently, the optical and electrical performance of the aforementioned topography was studied as a function of nanopillar height. The observations indicate that the electrical performance of the produced devices degrades with increases in nanopillar height beyond 800 nm, however, the optical performance measurements did exhibit the opposite trend. Upon the incorporation of metallic nanoparticles to the previously fabricated nanopillar arrays, the power conversation efficiency of the combined structure was observed to decrease to 7.31%. This can be attributed due to a reduced open circuit voltage in spite of having a higher fill factor.

1. Introduction

In recent years, there has been an increased interest in novel solar cell device architectures with the possibility of low cost, high efficiency and large scale integration [1,2]. Effective light trapping is crucial for producing high efficiency solar cell devices; this can be achieved by allowing weakly absorbed light to undergo multiple reflections within the cell either by employing thin film back reflectors, surface texturing or nanoparticle plasmonics effects. The latter scheme for light trapping has been extensively studied both theoretically and experimentally [3–8], and it has the potential to reduce the physical thickness of solar cells by maintaining the optical thickness constant, due to the two basic reasons, namely, (i) the metallic nanoparticles can be used as sub-wavelength scattering elements to couple and trap freely propagating light wave into the substrate and, (ii) the metallic nanoparticles can be used as sub-wavelength antennas in which the plasmonics near field is coupled to the substrate, increasing its effective cross-section area. Several groups have studied the plasmonics light scattering properties of metal nanoparticles both in front and rear sides of the cells to increase the optical absorption and hence, the efficiency of silicon based solar cells [5,7–9]. However, to the best of our knowledge none of them have shown actual efficiency enhancement compared to state of the art solar cells, despite having promising theoretical results. Similarly, sub-wavelength nano-texturing has received great attention due to its unique optical and electrical properties. Excellent light absorption and hence, a better electrical performance of silicon nanostructure such as silicon nanowires (*SiNW*), silicon nanopillars (*SiNP*), silicon nanoholes (*SiNH*), etc. have been demonstrated both theoretically and experimentally [10–13]. Furthermore, radial p–n junction structures composed of vertically aligned nanopillar arrays have attracted a great deal of attention because they may allow solar cell fabrication with materials having short minority carrier diffusion lengths by decoupling the light absorption and carrier extraction into orthogonal spatial directions. Radial junction nanostructured solar cells have experienced significant improvements in recent years, and different groups have reported efficiencies close to 10% [14–18]. In this paper, we propose a new solar cell design consisting of a radial p–n junction silicon nanopillar arrays in combination with plasmonics metallic nanoparticles resolved at the top of the nanopillars. This scheme has the potential of enabling lower-cost photovoltaic devices.

2. Experimental details

Wafer scale highly ordered *SiNP* arrays were fabricated by metal assisted electroless chemical etching (*MAECE*) in combination with colloidal lithography (*CL*). Four inch p-type silicon (100) wafers with a resistivity of 1–10 Ω-cm were cleaned using a piranha solution (an aqueous solution of 30% H_2O_2 and, conc. H_2SO_4 with a volume ratio of 1:3) at 90 °C for 10 min followed by a rinse in DI water and dried with a stream of nitrogen. The wafers were then

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immersed in an *RCA* solution (an aqueous solution of 30% H_2O_2, conc. NH_4OH and, DI water with a volume ratio of 1:1:5) at 80 °C for 30 min to obtain a hydrophilic silicon surface. Polystyrene (*PS*) nanoparticles of size 650 nm in an aqueous solution (5065B, Duke Scientific, Palo Alto, CA) was mixed with methanol and Triton X-100 (surfactant) with a volume ratio of 200:200:1. A 1.5–2 ml of suspension of *PS* nanoparticles was spin-cast on the silicon substrate. The spin coating was performed at the rate of 300 rpm for 30 s, 800 rpm for 120 s and 1400 rpm for 30 s to arrange the *PS* nanoparticles uniformly on the sample. The coated sample was placed on a hot plate and baked at 50 °C for 5 min to remove the organic solvent. A commercial barrel etcher was employed to reduce the size of the *PS* nanoparticles utilizing an $O_2 + CF_4$ plasma with flow rates of 200 sccm and 10 sccm, respectively, with a chamber pressure of 200 mT while applying 200 W of RF power for 5 min. Subsequently, a 40 nm gold (Au) film was deposited on the *PS* coated sample by using a commercial table top sputter coater. The honeycomb-like Au pattern on silicon was created by the liftoff of the *PS* particles. The highly ordered *SiNP* arrays were fabricated by immersing the sample in an etching solution consisting of HF, H_2O_2 and H_2O with a volume ratio of 25:10:75. The mechanism of *MAECE* can be found elsewhere [19–22]. This can be succinctly explained as a galvanic displacement of Au induced local oxidation and subsequent dissolution of silicon. The etching mechanism can be summarized as follows:

Cathode reaction at the metal :

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$$

$$2H^+ + 2e^- \rightarrow H_2$$

Anode reaction at silicon surface :

$$Si + 2H_2O + 4h^+ \rightarrow SiO_2 + 4H^+$$

$$SiO_2 + 6HF \rightarrow H_2O + H_2SiF_6 + H_2O$$

The overall reaction :

$$Si + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2$$

The Au layer adhering to the silicon surface has a greater electro-negativity than silicon. Therefore, the electrons from the silicon atoms are attracted to the Au atoms making the Au layer negatively charged. Furthermore, the negative oxygen (O^-) ions from H_2O_2, capture electrons from the negatively charged Au layer and become O^{2-} ions. This charge transfer causes the local oxidation of the silicon underneath the Au pattern. The produced silicon dioxide (SiO_2) is then continuously etched away by HF, leading to the penetration of the whole Au pattern into the silicon surface forming the *SiNP* arrays structure. The under laying gold film was removed by immersing the sample in a gold etchant (651818 from Sigma–Aldrich Inc.) solution for 30 min. The samples were examined by using high resolution scanning electron microscopy (Hitachi S-5500). The optical reflectance spectra measurements were performed by using a *UV–VIS–NIR* (Varian cary-5000) spectrometer equipped with integrating spheres. The spin on dopant (*SOD*) solution was prepared by the sol–gel method, mixing 5 gm of phosphorous pentaoxide (P_2O_5), with the solution of tetraethoxysilane (TEOS), ethanol (C_2H_5OH) and DI water in the volume ration of 1:2:1 at 80 °C for 60 min. The *SOD* solution was spin coated on the silicon nanopillar arrays textured surface to form a conformal coating on it. The samples were baked at 120 °C for 30 min to remove the organic solvents and subsequently fired at 870 °C in a high temperature furnace for 10 min for the radial p–n junction formation. The parasitic silicate glass layer was then removed by immersing the sample in an HF (2%) aqueous solution for 120 s. The doping level was measured by using a four point probe tool. The average sheet resistance of the *SiNP* arrays textured sample was observed to be 70 Ω/sq. A thin layer of dry SiO_2 was grown at 900 °C for 30 min to passivate the *SiNP* arrays textured surface. The front side nickel (80 nm)/silver (400 nm) finger electrode was fabricated by conventional photolithographic techniques. The back side metal electrode was formed by coating the back surface of the sample with an aluminum paste (AL5130V, Ferro Corporation, CA). The sample was subsequently fired at 750 °C for 5 min to form the back surface field (*BSF*). The schematic fabrication processes of the *SiNP* arrays textured solar cells are shown in Fig. 1. To include the front side Au plasmonics effect, a 35 nm gold

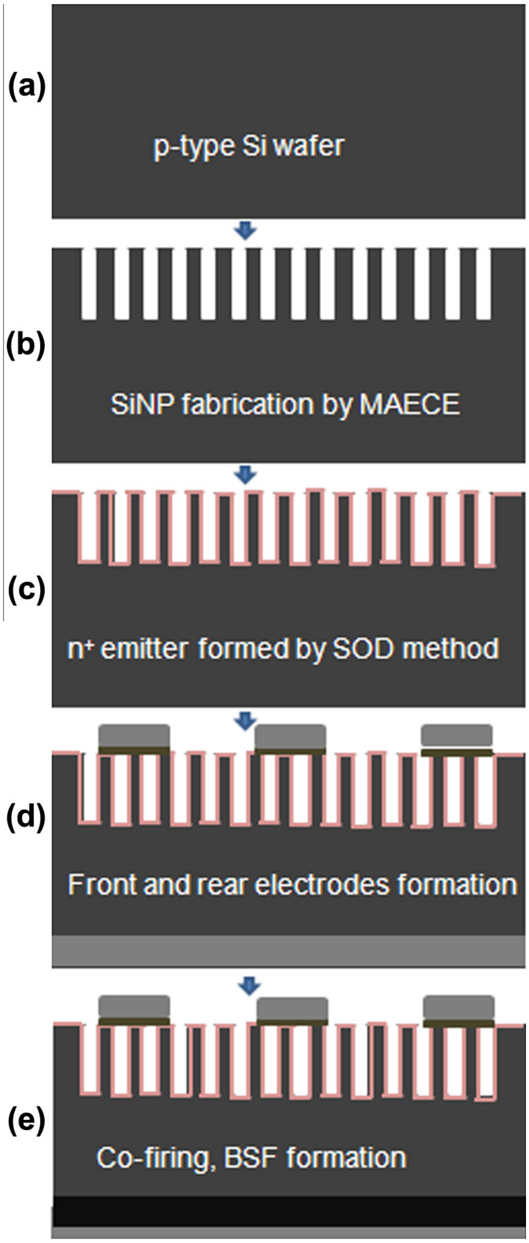

Fig. 1. Schematic of fabrication processes of radial junction *SiNP* arrays textured solar cells. (a) 1–10 ohm-cm p-type CZ silicon wafer, (b) fabrication of *SiNP* arrays by MAECE method, (c) radial p–n junction formation by SOD technique, (d) Ni/Ag front and Al back electrodes formation, and (e) back surface field (BSF) formation by firing the sample at 750 °C for 5 min.