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Viewpoint Paper

Hybrid gold/porous silicon thin films for plasmonic solar cells

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Abstract—We present here a study on the viability of using gold nanoparticles infiltrated into porous silicon (PS) to develop plasmonic thin-film solar cells. For this objective, hybrid structures consisting of PS thin films and gold nanoparticles were fabricated. Optical, electrical and photocurrent measurements were carried out, from which it was found that the presence of gold nanoparticles in PS results in increased responsivity. This effect can be associated with increased light absorption and increased carrier collection efficiency.

Keywords: Porous silicon; Plasmonics; Photocurrent; Responsivity; Solar cell

1. Introduction

Given the abundance of silicon in the earth's crust, together with its long-term stability, well-established technology (which has its origins in the semiconductor industry), and relatively low cost, silicon is likely to remain the dominant photovoltaic material for the foreseeable future [1]. Silicon thin-film solar cells have attracted much attention mainly due to a significant cost advantage over their bulk crystalline counterparts. In fact, around 40% of the cost of a solar module made from crystalline silicon is the cost of the silicon wafers [2]. However, a major problem with Si thin-film solar cells is related to ineffective light absorption, caused by Si being an indirect band gap semiconductor, and low carrier collection efficiency due to short carrier diffusion lengths [3].

In order to increase the overall efficiency of thin-film solar cells, boosting light absorption while still keeping the active layer thin would be an optimal solution. One attractive method to achieve this objective is to take advantage of light scattering from metal nanoparticles near their localized plasmon resonance frequency [2]. Plasmon resonance involves a collective oscillation of the conduction electrons in the metal. Incident light of wavelength close to the resonance wavelength of metal particles is strongly scattered or absorbed depending on the size, shape and material of the particles, as well as on the refractive index of the surrounding medium [4]. Accordingly, light absorption can be enhanced by engineering of metallic nanostructures [5], which is a key factor in the case of thin-film solar cells. Photon absorption can be increased by optimizing the coupling between the absorbing layer and incident light, especially in the spectral range where a given material shows weak absorption [6]. Photocurrent generation has been experimentally found to improve by placing or scattering metallic nanoparticles on top of, within, or at the bottom of photovoltaic devices [5].

The morphology and physicochemical properties of porous silicon (PS) greatly depend on the fabrication process and materials [7]. In particular, pore dimensions can be precisely controlled and are highly tunable from sizes below 2 nm to several microns [8]. Additionally, porosity has been reported to vary from about 1–95% [9]. Moreover, unlike any other porous material, patterns of porosity can also be generated laterally and vertically. Electrochemical etching of monocrystalline silicon wafers in HF-based solutions is the most widely used and versatile method for the fabrication of PS. Given its good optical properties, PS has been used in a wide range of photonic applications (e.g. [10,11]). In addition to its tunable properties, the relatively simplicity and low cost of PS processing make PS a promising material for use in solar cells. However, PS has seen limited applications in the field of photovoltaics and has been mainly used as an antireflection coating in silicon-based solar cells [12–15].

In this work hybrid structures consisting of PS thin films and gold nanoparticles were fabricated by a combination of electrochemical etching and electrodeposition.

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The electrical and optical behavior of these structures was determined. Additionally, the spectral behavior of the photocurrent generated by these devices was measured, from which the spectral responsivity was determined.

2. Experimental

2.1. Fabrication

Aluminum thin films (about 1 μm thick) were deposited by electron beam evaporation on the back side of boron-doped (p-type) monocrystalline Si wafers (orientation ⟨100⟩ and resistivity 0.01–0.02 Ω cm). In order to create low-resistivity ohmic contacts, annealing at 400 °C for 5 min was performed. PS thin films were fabricated by the electrochemical etching of silicon wafers into 48 wt.% HF:ethanol (1:2 v/v) solutions. The anodization time was 4 s under a constant current density of 60 mA cm^{-2}.

Electrodeposition of gold nanoparticles into PS was performed immediately after the formation of the porous thin films following an experimental method previously described [16,17]. For this task, a solution consisting of $HAuCl_4$, 0.42 M $Na_2S_2O_3$ and 0.42 M Na_2SO_3 was used. The $HAuCl_4$ concentration was 1 mM, the current 1 μA cm^{-2} and the duration of the immersion/deposition step was either 60 and 600 s. The overall fabrication process results in hybrid Al/Si/PS + Au structures, which are named Al/Si/PS + Au(60 s) and Al/Si/PS + Au(600 s), depending on the length of the immersion/deposition step.

Finally, semitransparent indium tin oxide (ITO) layers were grown on top of the PS thin films by magnetron sputtering, at a typical pressure of 5×10^{-3} torr. The sputtering time was fixed at 60 min, resulting in layers typically 0.5 μm thick. After the deposition process, the structures were subjected to rapid thermal processing at 550 °C for 600 s in vacuum in order to improve the conductivity and transparency of the ITO layers.

The previously described process results in a four-layer structure schematically depicted in Figure 1.

2.2. Characterization

Scanning electron microscopy (SEM) images of the different structures were obtained using a Philips XL30 S field emission microscope operated at 10 kV.

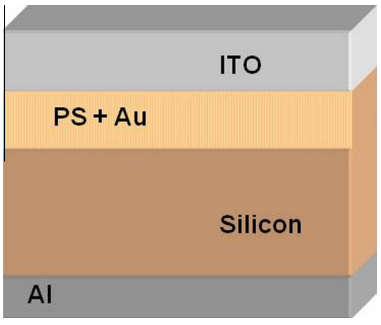

Figure 1. Schematics of the four-layer structure of the PS-based plasmonic devices: Al/Si/PS + Au/ITO structures.

Electrical characterization, i.e. measurement of the current–voltage (*I–V*) curves, was carried out in the dark by using a Hewlett Packard pA meter/DC voltage source, Model 4140B. The reflectance spectra in the 350–900 nm wavelength range were taken using a Jasco V-560 double-beam spectrophotometer equipped with an integrating sphere, which avoids scattering losses. The photometric accuracy was better than 0.3%.

Photocurrent measurements were carried out at 0 V bias using a dual digital lock-in amplifier (Signal Recovery 7225) at a chopper frequency of 300 Hz. Illumination was provided by an Acton Research Corporation Tungsten-Deuterium dual light source (Model TDS-429) and a SpectraPro 150 monochromator equipped with three interchangeable diffraction gratings (1200 lines mm^{-1}) was used to select the wavelength.

3. Results and discussion

Field-emission scanning electron microscopy (FESEM) was used to directly analyze the morphology of the PS thin films and ITO layers, as well as the characteristic dimensions of the gold nanoparticles electrodeposited into the porous structure. For this purpose, the structure of the samples was analyzed at different stages of the fabrication process. Figure 2(top) shows a cross-sectional view of the typical morphology of PS layers before electrodeposition of gold nanoparticles.

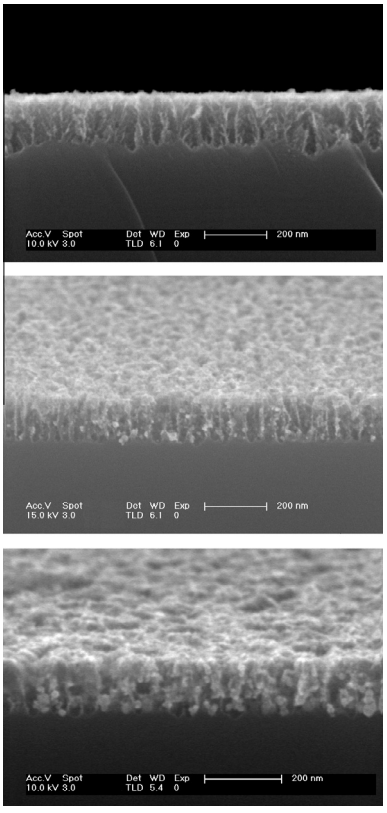

Figure 2. Cross-sectional FESEM images of (top) a PS thin film, (middle) PS with gold nanoparticles deposited for 60 s, and (bottom) PS with gold nanoparticles deposited for 600 s.