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From random to order: Colloidal crystals on non-flat surfaces

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ABSTRACT

This paper introduces the possibility to produce 1–2 cm^2 and tens of layers colloidal crystals on different non-flat surfaces by means of electrospray deposition. Two different types of crystalline silicon surfaces were tested: nanostructured "black silicon" and random pyramids. Several trenches were drilled by SEM-FIB to assess the morphology of the samples. The results of these measurements show that an ordered and consistent structure can be obtained on both cases after some disordered layers. The relative aspect ratio between the features on the silicon surface and the nanoparticle defines whether the order/disorder interface follows the surface profile. Apart from checking the internal structure, the quality of the structures has been assessed by measuring the reflectance spectra showing a consistent reflection peak of 80% at 950 nm, as expected from the size and structure on the nanoparticles.

1. Introduction

Colloidal crystal structures have been intensively studied in the last 20 years due to their sophisticated photonic properties, like selective light scattering and optical filtering, combined with relatively low-cost techniques for their fabrication [1–11]. This last characteristic makes them attractive to be included in optoelectronic devices where the cost is playing a crucial role. For example, this type of structures has been applied to improve light trapping in photovoltaic cells and thermophotovoltaic devices [12–14]. Focusing on crystalline silicon (c-Si) solar cells, the reduction of device thickness makes light trapping schemes of paramount importance to keep light absorption at the same level than thick devices. The technologies used to create colloidal structures have been typically based on flat surfaces, mainly glass or polished silicon [15]. Besides, most of these technologies were restricted to very small areas, which limited their use in real devices. On the other hand, if we focus on real photovoltaic and optic devices, they are usually fabricated onto non-flat surfaces, e.g., pre-texturized surfaces, non-polished surfaces or even surfaces with gratings. Additionally, they have relatively high areas (more than 1 cm^2). These constraints of flatness and active area result in a much harder definition of any ordered nanostructure on such surfaces. Most of the techniques used nowadays are not efficient enough to provide big area structures of several layers of colloidal crystals with enough quality and certainly all the technologies used today are only applicable on flat surfaces [15].

Recently, a technology developed in our group based on electrospray colloidal deposition [16–18] has been added to the repertoire of techniques used to create these colloidal crystal structures with the advantage of covering big areas. This technique uses an electrospray source to ionize the liquid with colloids and, by means of electrowetting and surface tension forces, order the nanoparticles creating 3D arranged large area colloidal crystals. Lately, the electrospray deposition technique has also been used to create a scaffold for inverse opal structures [19]. Taking advantage of the big area coverage, a proof of concept of solar cell back reflector has been tested assuring that the electrical and the mechanical properties of the crystalline silicon were kept constant [20].

All the previous attempts of using this technique were applied on flat surfaces, either glass, polished silicon or evaporated metals on top of this surfaces. In this paper we explore the formation of 3D colloidal crystals by this electrospray deposition technique in uneven surfaces. This possibility opens a new range of applications to photovoltaic devices and, in particular to thin crystalline silicon solar cells.

2. Experimental

To analyze the viability of creating colloidal crystals onto unevenness surfaces two different samples have been used. Firstly, we used a random pyramid textured c-Si surface which is the common surface that can be found in industrial c-Si solar cells. Secondly, we used a nanostructured crystalline silicon surface known as black silicon. Random nanopillars of about 800 nm tall and 200 nm width are defined onto the c-Si surface (see Fig. 2(a)) in order to drastically reduce c-Si reflectivity. Although this surface treatment has not been applied to commercial solar cells yet, lab-scale solar cells with very high shortcircuit currents have been fabricated demonstrating its potential for high efficiency devices [21]. The black silicon surface is achieved by etching both wafer surfaces through a cryogenic inductively coupled plasma reactive-ion etching process (ICP-RIE) at −120 °C using SF6 and O_2 as

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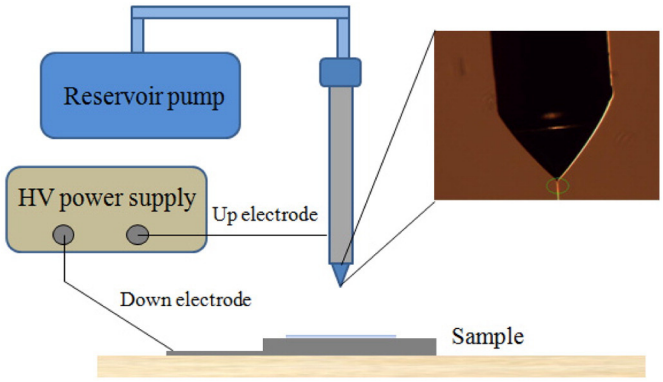

Fig. 1. Electrospray deposition setup: Schematic description of the setup that composes the electrospray deposition with a close view of the needle's tip, the Taylor cone and the resulting liquid jet.

etching gases. On the other side, the random textured sample is formed by etching the silicon with TMAH at 70 °C. In addition, a flat crystalline silicon surface is also used as a reference.

The first step of the fabrication process is to prepare the surfaces for the deposition, dipping both black silicon and the random pyramids samples into a 2% solution of hydrofluoric acid. The deposition of the nanoparticles is performed by electrospraying the nanofluid solution consisting of distilled water and 360 nm polystyrene nanoparticles with a concentration of 25 mg/ml. The setup used to electrospray the nanoparticles includes an infusion pump from B. Braun SA (Melsungen, Germany), an OMNIFIX (Braun) 5-ml syringe and a Hamilton needle (600-μm outer diameter and 130-μm inner diameter). A potential difference in the order of 5 kV is necessary to perform the experiments. As an up electrode, a needle is polarized at several kilovolts using an Ultravolt high-voltage bipolar source, (Ultravolt, Ronkonkoma, NY, USA). The other electrode is placed on the substrate of the sample and it is polarized at −500 V. The distance between the sample and the needle was fixed at 2 cm. A schematic view of the setup could be seen in Fig.. 1.

The characterization of the samples includes optical measurements of the reflectance using a Shimadzu (Kyoto, Japan) UV3600 UV–VIS–NIR spectrophotometer and an ISR-3100 integrating sphere attachment of 3 mm × 12 mm beam area. SEM pictures have been made to supervise and control the topology of the colloidal crystals, analyzing the existence of 3D order, the amount of layers involved in the ordering phase and the transition between the first non ordered layers and the promoted order.

3. Results and discussion

Colloidal crystals were fabricated onto both black silicon and texturized surfaces. Focusing on the former, we made some FIB trenches in order to analyze the order promotion from the c-Si surface to the top of the colloidal crystal. As it can be seen in Fig. 2, b), the colloidal crystal formed on top of this structure is composed of tens of layers, most of them ordered, but the initial phases are disordered. Exploring the area in between the black silicon and the colloidal crystal, some disordered layers were found mainly due to the geometric impossibility to produce a first ordered monolayer at the interface of the silicon, as could be seen in Fig. 2, b). Notice that the interface of the ordered and disordered regions indicated by a green line is flat and parallel to the surface of the sample. We attribute this characteristic to the fact that the irregularities of the surface sample are comparable in size to a nanoparticle being quite unlikely that a particle gets stuck between two nanopillars.

Moving on random pyramid texturized c-Si surfaces, we applied identical experimental conditions to create the colloidal crystal. Again, the structure was measured by SEM-FIB leading to pictures shown in Fig. 3. A similar organization than in the black silicon case is observed with a certain disordered region close to c-Si surface. The main difference between both surfaces is that on texturized surface the interface between the ordered and disordered regions is not flat. In fact, it replicates the surface profile contour formed by the pyramids. This can be clearly seen in Fig. 5, a) and b), where a green line indicates the ordered/disordered interface. Now, the irregularities of the surface sample are much bigger in height (3–5 μm) than a nanoparticle (360 nm in diameter) and the disordered region follows the c-Si profile. From these results, we can conclude that a minimum thickness of about 2 μm of this region is necessary to promote the order between nanoparticles.

The hypothesis behind this order created from random surfaces is the following. The aggregation of nanofluids on a flat sample could be regular from the surface due to the formation of an ordered 2D structure at the first layer, as shown in Fig. 4a. In the absence of this possibility, as it is the case on a non-flat surface, the nanoparticles tend to become disordered from the bottom to the top as shown in Fig. 4b. When the electrospray technique is used, an electric field appears in the surroundings of the nanoparticles during their deposition. The electrophoretic effect is added to the pure mechanical deposition promoting the order between nanoparticles [22]. Consequently, a colloidal crystal can be created after smoothing the surface as a result of the first disorder layers as sketched in Fig. 4, c.

Finally, with the objective of checking the optical performance of the fabricated colloidal crystals, reflectance of both samples was measured using the Shimadzsu spectrophotometer. The obtained results are

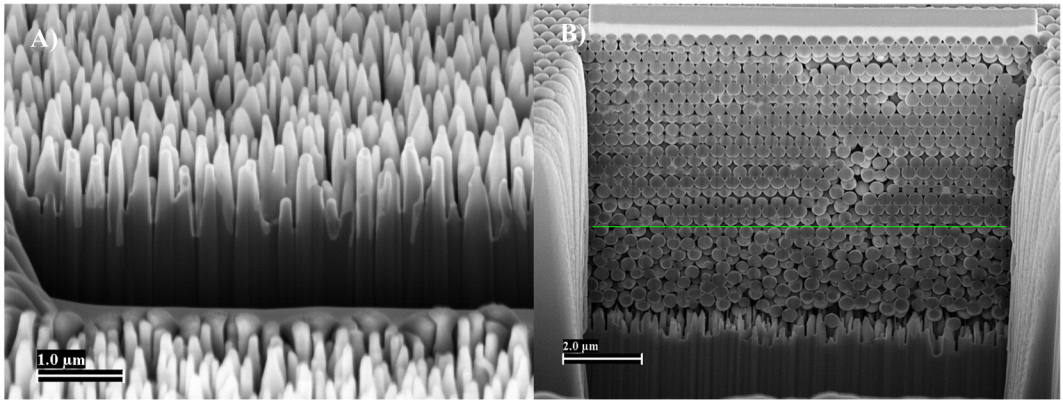

Fig. 2. SEM micrographs of colloidal crystals on top of black silicon: a) Top surface of the black silicon sample with small FIB trench that shows the shape of the nanopillars. b) General view of FIB trench showing clearly the two phases of nonordered and ordered nanoparticles.