Solar Energy Materials & Solar Cells 159 (2017) 640–648

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Optimization and optical characterization of vertical nanowire arrays for core-shell structure solar cells

Martin Foldyna [a,*], Alienor Svietlana Togonal [a,b,c], Rusli [b,c], Pere Roca i Cabarrocas [a]

[a] LPICM, CNRS, Ecole Polytechnique, Université Paris-Saclay, 91128 Palaiseau, France
[b] Novitas, Nanoelectronics Centre of Excellence, School of Electrical and Electronics Engineering, Nanyang Technological University, 639798 Singapore
[c] CINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 637553 Singapore

ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form
20 May 2016
Accepted 11 June 2016
Available online 2 July 2016

Keywords:
Silicon nanowires
Solar cells
Light trapping
Optical characterization
Performance optimization
Optical model

ABSTRACT

In this work we study optical properties of vertical silicon nanowire (SiNW) arrays fabricated using metal assisted chemical etching (MACE) coupled with nanosphere lithography (NSL). We have studied optimal configurations minimizing total reflectance of 2 μm long SiNW arrays by modeling and compared their performance with experimental data. Fabricated SiNW arrays have shown lower total reflectance than modeled perfectly periodic ones. This has been found to be due to a variation of NW geometry and the presence of domains caused by the self-assembly during NSL process. We have developed a statistical model (based on rigorous coupled wave analysis) describing geometry variations and also demonstrated that different domains have rotated diffraction pattern with respect to their symmetry axes. The statistical model has been successfully validated on total reflectance and normalized Mueller matrix data. Furthermore, we have found that a very high light trapping can be achieved for nanowires only 125 nm long (Jsc equivalent of up to 42 mA/cm^2), which can be exploited in thin and ultra-thin Si solar cells.

1. Introduction

At the present time, the majority of the photovoltaic market is dominated by crystalline silicon solar cells and modules based on that technology. In some places, the cost of the energy generated by photovoltaic panels is in the parity with the cost of the electricity from the grid [1]. While the cost of the modules has decreased significantly during the last few years [2], the goal of the photovoltaic industry is to further reduce the cost per watt and to make the renewable solar energy competitive with the energy from fossil fuels.

A significant part of the silicon solar panel cost is formed by the crystalline material, which has led to strong industrial efforts to develop technologies for handling of thinner wafers and attempts to further reduce their thickness [3]. However, the reduced wafer thickness does not reduce only cost, but also the absorption inside the silicon or more precisely the device performance. In order to reduce the impact on the performance, thinner crystalline silicon absorbers require more efficient light trapping than their thicker counterparts. In particular, it has been shown that silicon nanowires can be very efficient at light trapping [4,5] while also providing substantial material saving when compared to standard etched pyramids.

An important aspect of the nanostructured surface considered for the silicon photovoltaic devices is the possibility to fabricate those structures using an inexpensive method suitable for large areas. This can be accomplished for vertical nanowire structures by a combination of the suitable patterning technique and the metal assisted chemical etching (MACE) [6]. The main advantage of this etching technique is that it can be easily adopted on the large scale. Using MACE as it is leads to a random distribution of dense arrays of nanowires of randomly distributed diameters and positions. In fact, while such configuration may perform very well as an antireflective surface, its passivation is a very challenging task [7]. In order to better optimize the performance, a nanosphere lithography (NSL) has been used which does not require any precise positioning and forms naturally hexagonal short range ordering [8]. Such vertical nanowire arrays can be used for core-shell devices, where the efficient light trapping of nanowire arrays can be coupled with the high performance of heterojunction devices [9].

While this short range ordering might resemble the perfect organization, at closer look it reveals small imperfections such as varying distance between nanowires, the narrow distribution of the diameters and bottom interface between nanowires and crystalline silicon wafer possibly involving a surface modulation. All those structural imperfection have impact on the optical properties and the performance of the devices based on them.

---

* Corresponding author.
E-mail address: martin.foldyna@polytechnique.edu (M. Foldyna).

http://dx.doi.org/10.1016/j.solmat.2016.06.014

Therefore, for the optimization of the performance, more statistically accurate models of those structures are needed. Only such statistically accurate models can precisely describe the expected optical performance of such nanostructures and can be used for accurate optimization of solar cell devices.

In this work, we have modeled and fabricated vertical silicon nanowire arrays to evaluate optimal configurations suitable for photovoltaics. The samples were fabricated using the MACE process coupled with NSL. Fabricated samples have been characterized optically and the results compared with the periodic model at first. The distribution of fabricated nanowire diameters and surface roughness with surface porosity caused by the wet etching using HF and H_2O_2 solution has been taken into account by a new model developed for this purpose. This model has been compared with measured total reflectance and Mueller matrix data. The optical model, fabrication and characterization methods are explained in the second section, while the results are reported in the third section.

2. Sample fabrication, characterization and modeling techniques

2.1. Sample preparation

Silicon nanowire (SiNW) arrays studied in this work have been fabricated using MACE coupled with NSL which allows for a good control of nanowire distance, diameter and length. At first, crystalline silicon wafers [100] are cleaned in acetone, IPA and deionized water for 10 min each by an ultrasonic bath at room temperature. A monolayer of polystyrene spheres (PS) (provider is MicroParticles GmbH, Germany), with different nominal diameters between 250 and 800 nm, was used as an etching mask. Solutions of PS were mixed with ethanol (1:1) and ultra sonicated for 10 min. Afterwards, a PS monolayer was deposited on Si wafers using a floating–transferring technique. The initial diameter of PS determined the pitch (distance from the center to center) of the fabricated structure. Subsequently, PS were reduced by an oxygen plasma treatment, where etching time determined the diameters of the fabricated SiNWs. Afterwards, a thin 25 nm film of gold was deposited by e-beam evaporation. The PS were subsequently removed by immersing the sample into a toluene solution leading to the formation of a gold membrane with holes. A solution mixture of HF, H_2O and H_2O_2 was used during the etching procedure, where the nanowire (NW) length was controlled by the etching time. At the end of the etching process, the gold film was removed by potassium iodide, completing the fabrication of an array of SiNWs with a controlled geometry. The steps of this process are summarized in Fig. 1. Applying this fabrication process allows a good control over nanowire diameters, heights and center-to-center distances, which is critical for the optimization of their optical properties.

2.2. Optical characterization tools

In order to quantify the reflectance of fabricated samples, they have been characterized by using spectrophotometer (PerkinElmer) operating in the spectral range from 250 to 2000 nm. The typical spot size is between 4 and 15 mm^2. An integration sphere ensured that the total reflectance has been measured at the angle of incidence of 8°. Selected samples were also measured with a variable angle Mueller matrix polarimeter in a spectral range from 450 to 1000 nm and at the angle of incidence of 60° in order to provide more accurate estimates to nanowire geometry and improve sensitivity to e.g. surface roughness. The selected spot size in this case was $250 \times 250\ \mu m^2$ and all elements of the normalized Mueller matrix were measured at the specified wavelength range.

Domain structure coming from the nanosphere self-assembly step during the fabrication has been studied using angle-resolved Mueller matrix polarimetry (AR-MMP) tool. The main advantages of this setup are the measurement of complete Mueller matrices and the ability to operate in the Fourier (angle-resolved) and real-space (microscope) regimes. The important part of the setup is a microscope objective with numerical aperture of 0.95, which allows focusing the light on very small spots (between 5 and few tens of μm in diameter) and collect the light from wide range of incidence and azimuthal angles at once. The setup was operated with a 633 nm HeNe laser illumination, where the illuminating light has passed through a rotating depolarizer to provide high intensity unpolarized light illumination. The normal angle of incidence was controlled by a pinhole placed carefully in the center of the Fourier plane of the illuminating beam. More detailed description of the setup can be found in Ref. [10].

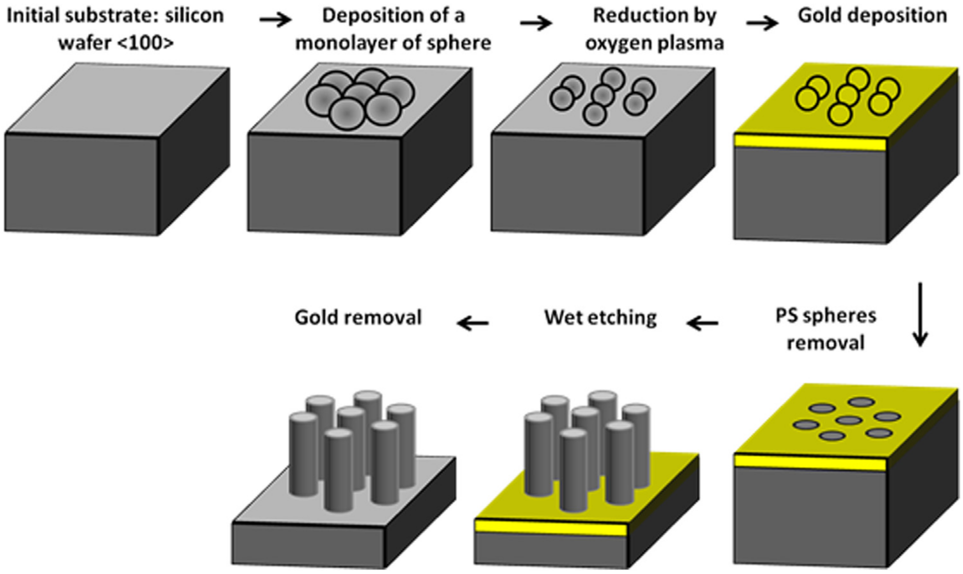

Fig. 1. The schematics of every step of a metal assisted etching (MACE) fabrication process coupled with nanosphere lithography (NSL).