Silver Nanoparticles Effect on Silicon Nanowires Properties

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Abstract

This work focuses on optical characterization of silicon nanowires (SiNWs) used for photovoltaic applications. We report on the elaboration of silicon nanowires by Metal Assisted Chemical Etching (MACE) technique using silver (Ag) as metal catalyst. The obtained results show that the SiNWs optical properties are sensitive to their elaboration conditions specially the cleaning protocol. The reflectivity was found to be dependent on wavelength and increased from ultra-violet to red wavelength for all tested samples. The comparison between samples with different cleaning protocol shows that, in the UV spectral region, SiNWs more contaminated with Ag nanoparticles present a pronounced decrease of the reflectivity. This optical behavior was attributed to metallic nanoparticles persisting in the silicon nanowires structures presenting surface plasmon resonance energy in a vicinity of UV spectral region.

Keywords

SiNWs, MACE, Reflectivity, Silver Nanoparticles, Surface Plasmon Resonance

1. Introduction

Silicon-based solar cells remain the main candidate in photovoltaic solar energy conversion [1]. However, a large part of the solar cell conversion-efficiency limits are attributed to the optical losses in silicon material. That’s why the scientific community is interested in developing concepts and technologies that enable reducing optical losses and thus enhance the solar cell efficiency [2-4]. Conventionally, the surface reflectivity of silicon-based solar cells can be reduced by texturing the front side of the cell [5-7] and/or using appropriate antireflection (AR) coatings [8,9]. During the last decade, important efforts have been dedicated to the use of silicon nanowires structures (SiNWs) in photovoltaic applications. SiNWs deposited on the surface of silicon-based solar cells could act as an efficient antireflection layer. Such structures present highly light absorption behavior which could attain 97% in UV-visible spectral regions attributed to light confinement of incident light in the nanowires structures, as for porous silicon. Nowadays, silicon nanowires have been integrated in many other devices and applications such as silicon nanowire field-effect transistor (SiNW-FET) in microelectronics applications and biological sensors thanks to their high internal surface [10,11]. Many techniques are proposed in order to elaborate homogenous silicon nanowires: bottom up and top down approaches. One of the mostly used methods in the bottom up approaches is the vapor Liquid Solid (VLS) method which needs the use of hard equipments like the CVD or PECVD. In this work, we have elaborated silicon nanowires with a top down method: the Metal Assisted Chemical Etching (MACE). This method is simple and can lead to homogenous silicon nanowires. Gold and silver are the most used metals as catalysts. Gold is known to diffuse and create deep-level defects in the silicon band gap [12]. These defects act as recombination centers deteriorating the electrical properties of
2. Experimental Details

To elaborate silicon nanowires, the substrates used are boron-doped single crystalline silicon (100) with a resistivity of ~1-3 ohm.cm and a thickness of 300 µm. Before SiNWs elaboration, silicon substrates were cleaned with acetone for 1 min followed by immersion in ethanol for 1 min and rinsed in deionized water in order to eliminate organic greases. Finally, the substrates are etched in 5% HF for 1 min to eliminate native oxide. Silicon nanowires were prepared by Metal Assisted Chemical Etching technique (MACE). The method used is one-step process consisting of silver nanoparticles deposition and silicon etching (Fig.1 (a)). The silicon substrates are immersed in a mixture of 10 ml HF (48%), 10 ml AgNO$_3$ solution and 1 ml H$_2$O$_2$ (30%) at room temperature for 40 min. At the end of the experience, the substrates are covered by a thick silver layer, the dendritic layer, which has an important role in the etching mechanism (Fig.1 (b)) [13,14]. Finally, the substrates are rinsed with water to stop the etching and then rinsed with nitric acid (HNO$_3$) to eliminate silver (Fig.1(c)). The surface reflectivity of elaborated SiNWs was analyzed using a PerkinElmer Lambda 950 UV/VIS spectrometer. The morphological features of SiNWs were investigated using a JEOL JSM-5400 Scanning Electron Microscopy (SEM).

3. Results and Discussion

3.1. Silicon Nanowires Elaboration in HF/AgNO$_3$/H$_2$O$_2$ Solution

The elaboration of silicon nanowires by MACE consists on metal nanoparticles deposition and silicon etching. Metal nanoparticles are deposited by Electroless Metal Deposition (EMD) which is a commonly used technique for metal-plating from a solution containing chemical reducing agents. Many research works have explained the formation of silicon nanowires by different mechanisms and have attributed different roles to metal nanoparticles depending on the process used and the experimental results. Qui et al. have proposed a chemical etching mechanism by using Ag-Nps [15]. They have suggested that Ag-Nps are protecting silicon during etching. Their conclusions are based on SEM characterization and X-ray analysis showing the presence of Ag-Nps on the top of SiNWs. However, Peng et al. were confused about the role of silver. In 2003, they explained that silver nanoparticles protect the silicon during etching [16] but later in 2005, they suggested that Ag-Nps are catalyzing the nanowires formation [17]. Bai et al. have also proposed that silicon nanowires formation in HF/AgNO$_3$/H$_2$O$_2$ solution is catalyzed by silver nanoparticles [13]. Our experimental results confirm the catalytic role of silver nanoparticles which cover the sidewalls of the formed SiNWs. In fact, silicon nanowires are elaborated in HF/AgNO$_3$/H$_2$O$_2$ solution. The first reaction consists on the capture of electrons by Ag$^+$ ions from silicon surface leading to Ag atoms and then to Ag nanoparticles deposition (Eq. 1). The second reaction is dealing with silicon etching by the formation and dissolution of silicon oxide. The total reaction is depicted by (Eq. 2).

\[
Ag^+ + e^- \rightarrow Ag(s) \quad \text{(Eq. 1)}
\]

\[
Si + 2Ag^+ + 6F^- + 2H^+ \rightarrow SiF_6^{2-} + 2Ag + H_2 \quad \text{(Eq. 2)}
\]

Fig. 1. (a) Schematic illustration of the formation of SiNWs in HF/AgNO$_3$/H$_2$O$_2$; (b) image of SiNWs sample covered by a dendritic layer; (c) image of SiNWs sample after elimination of the dendritic layer.

Fig. 2. SEM image of a silver dendritic layer.
As the etching time increases, a lateral growth of silver nanoparticles is occurring leading to a dendritic layer. Fig. 2 presents a SEM image illustrating this layer at the silicon surface showing the agglomeration of Ag-Nps. The presence of H₂O₂ in the etching solution may oxidize the dendritic layer generating more Ag⁺ ions in the solution. Despite the fact that dendritic layer is known to be transparent to Ag⁺ ions, its oxidation by H₂O₂ even with small amounts permits the formation of homogeneous SiNWs. Ag⁺ ions, going through the dendritic layer, oxidize silicon successively etched by HF. These two reactions continue until the formation of quasi-regular SiNWs covered by silver dendrites (Fig. 1(a)). This layer is eliminated by the reactivity of nitric acid with silver structure following (Eq. 3).

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O \quad (Eq. 3)$$

Fig. 3. SEM cross-section view of SiNWs formed in HF/AgNO₃/H₂O₂ solution during 40 min.

Fig. 4. SEM cross-section view of SiNWs showing the presence of silver nanoparticles.

Fig. 3 shows a cross-section SEM view of the obtained SiNWs with a length about 15 µm after the dendritic layer dissolution. Fig. 4 presents a magnification of the SiNWs illustrating the presence of Ag nanoparticles on their sidewalls. This observation confirms the catalytic effect of silver during silicon etching [13].

### 3.2. Optical Behavior of Silicon Nanowires

In order to investigate optical behavior of silicon nanowires, we have studied their reflectivity. In Fig. 5(a), we compare the reflectivity of silicon substrate with a SiNWs sample. We notice that the SiNWs decrease the total reflectivity as regards to the bare silicon thanks to light trapping by multiple reflections on SiNWs lateral surfaces. SiNWs reflectivity is wavelength dependent reaching its minimum in the UV spectral region. This behavior observed may be attributed to Ag-Nps. Silver nanoparticles are known to exhibit a plasmonic effect and present surface plasmon resonance energy in the UV spectral region [18] when illuminated by light with suitable wavelengths. This effect is a consequence of the oscillation of the conduction electrons of the metal under excitation enhancing the electric field leading to an absorption increase and then to a reflectivity decrease [19]. As mentioned above, Ag-Nps are found to be on the bottom and on the sidewalls of SiNWs even after silver dendrites elimination (Fig. 4). To confirm these observations; we have investigated the sensitivity of SiNWs optical response with the cleaning protocol. In Fig. 5(b), we compare the total reflectivity of SiNWs cleaned in a concentrated HNO₃ solution during 1 min (sample A) and SiNWs cleaned in diluted solution (<HNO₃:H₂O> <1:1>) during 1 min (sample B). Sample B, suspected to be more contaminated with Ag-Nps, exhibits a pronounced decrease of the reflectivity in the UV spectral region compared to sample A. Fig. 6 shows cross-section SEM images of sample A (Fig. 6(a)) and sample B (Fig. 6(b)). We observe that sample B presents effectively a higher density of Ag-Nps than sample A. These results support the hypothesis of metallic nanoparticles contribution on SiNWs optical response.
To confirm this behavior, we studied the reflectivity of the dendritic structures. Fig. 7 shows the surface reflectivity of three dendritic layers presenting different densities ($D_1 > D_2 > D_3$). We notice that the curves' shape is similar to those obtained for SiNWs structures. The reflectivity of different layers is a wavelength-dependent decreasing from visible to ultraviolet wavelengths. It exhibits a sharp drop around 350 nm reaching a minimum in the UV region. The drop observed is related to the optical response of Ag-Nps in the UV spectral region attributed to the plasmonic effect. This optical response presents an evidence of silver nanoparticles contribution in SiNWs reflectivity.

4. Conclusions

In this work, we have presented the elaboration of silicon nanowires structures that could be integrated in silicon-based solar cells as antireflection layer. SiNWs are formed by chemical etching technique assisted by silver. We reported a detailed study on the effect of silver nanoparticles on the optical response of silicon nanowires. These nanoparticles are persisting in the structure even after cleaning with HNO$_3$ and are influencing the SiNWs reflectivity. They present a plasmonic effect when excited by light leading to a reflectivity decrease. This property of Ag-Nps seems to be interesting in order to verify the efficiency of the cleaning protocol.

References


