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Effect of Silver-Assisted Chemical Vapor Etching on morphological properties and silicon solar cell performance

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ABSTRACT

In this work, we report a novel, simple and reproducible etching technique named Silver-Assisted Chemical Vapor Etching method (Ag-ACVE). It consists to expose Ag-loaded silicon substrates to vapors emanating from HF/H_2O_2 hot solution. The surface treatment performed with this method aims to enhance both optical and electrical properties of conventional silicon solar cells. SEM images of Ag-ACVE treated samples exhibit the appearance of porous micro-cavity like-structure for short etching duration. For long etching duration, sporadic and curved silicon nanowires (SiNWs) were formed. A kinetic study of the vapor etching reaction revealed a relatively high etching rate. Furthermore, the dimension of the micro-cavities increased as a function of the H_2O_2 molar ratio. UV–Visible measurement showed a significant decrease of the total reflectivity versus the molar ratio. Whereas, at the same time the minority carrier life time was significantly enhanced and as a result the solar cell performance was improved.

1. Introduction

Surface treatment is one of the most important silicon (Si) solar processing step aiming to reduce simultaneously the optical losses of incident light and the surface photo-generated carrier recombination velocity [1]. In addition to conventional alkaline-based texturization [2], two main methods are used as a complimentary surface treatment. The first consists in deposing simple or double anti-reflection coating layer (ARC) with an intermediate refractive index [3]. The second is the formation of a porous layer with different shape and thickness as an efficient trapping [4]. The formation of porous silicon (pSi) have been performed by several methods such as electrochemical anodization [5], stain etching [6], chemical vapor etching (CVE) [7] and metal assisted chemical etching (MACE) in the liquid phase [8,9]. MACE has recently attracted substantial attention since it permits a simple and low cost elaboration of controllable 1 and 2-D patterns [10]. The morphology of these patterns is affected by varying different parameters. Some of them are related to the etching condition such as HF-oxidant molar ratio [11] and etching duration [12]. Others parameters are related to the wafer specification such as doping level [13] and orientation [14]. Recently, Hildreth et al. [15] have used a new method by combining the MACE and the CVE techniques to produce macro-porous silicon. It consists in exposing metal coated Si substrates to acid vapors emanating from HF/H_2O_2 mixture. The formation of Si microstructures using HF/H_2O_2 vapors requires the stepwise oxidation of Si atoms followed by the formation of water soluble complexes (SiF_6^{2-}, $H_2SiF_6^{2-}$...). This process should enable the fabrication of even higher aspect ratios and with strong mechanical properties. Furthermore by using the Au as a catalyst in metal assisted chemical vapor etching (MACVE), Díaz-Torres et al. [16] have produced a microporous structure on the whole surface with a porosity gradient and thickness proportional to the etching time.

However, the effect of MACVE on Si optoelectrical properties and the solar cell performance is not been investigated. In this paper, we focus our attention on the effect of varying etching duration and HF/H_2O_2 molar ratio on morphologic and optoelectronic properties of silicon. In addition, we study the effect of the surface treatment by the Ag-Assisted Chemical Vapor Etching (Ag-ACVE) on the solar cells characteristic parameters.

2. Experimental details

2.1. Synthesis of Si micro-structure

The Si substrates used here have a surface area of 4 cm^2 (2 cm × 2 cm) and a thickness of 450 μm. These substrates are cut from the

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same boron doped Si wafers having a resistivity of 0.5–3 Ω cm. First, the substrates are cleaned in an acid solution mixture of HNO_3: 64%, HF: 16%, CH_3COOH: 20% for 30 s, then rinsed in deionized water. Secondly, they are immersed in an aqueous solution of 4.8 M HF (40 wt%) and 0.02 M $AgNO_3$ for 60 s to form Ag nanoparticles (AgNPs) by Electroless Metal Deposition (EMD). Then, the Ag-coated substrates are exposed to acid vapors, issued from an acid hot solution mixture of HF/H_2O_2. The acid solutions are characterized by their molar ratio $\rho_{H_2O_2} = \frac{[H_2O_2]}{[HF].+ \quad [H_2O_2]}$. The temperature of the acid solution and the distance between Si substrate and surface acid solution are maintained at 60 °C and 5 cm, respectively.

In order to study the kinetic reaction of the Ag-ACVE, the etching is experimented on six Ag-coated substrates at different durations 5, 20, 40, 60, 80 and 100 min at a fixed molar ratio $\rho_{H_2O_2}$=90%. These samples are named A_5, A_{20}, A_{40}, A_{60}, A_{80}, and A_{100}, respectively. In the second part, Si etching is performed on six other Ag-coated substrates at different molar ratios: 0%, 10%, 30%, 50%, 70% and 90%, during 60 min. These samples are named B_0, B_{10}, B_{30}, B_{50}, B_{70}, and B_{90}, respectively.

After etching the as-prepared samples are immersed in concentrated nitric acid (HNO_3) to remove AgNPs, rinsed with deionized water and dried. Table 1 gives a detailed summary of the etching conditions.

2.2. Solar cell processing

The effect of the Ag-ACVE on c-Si solar cells performance was analyzed using the current–voltage *J(V)* characteristic at AM 1.5. These treated samples are compared to a reference cell where the base substrate was not etched. The c-Si solar cells are achieved by performing phosphorus diffusion in a conventional furnace at a temperature of 930 °C during 20 min. The metallic contacts are made by thermal evaporation under vacuum of Al the rear contacts and Ag for the emitter contacts. The metallic contacts are separately annealed in an infrared furnace at 550 °C and 450 °C, respectively. Different experimental steps of Si micro-cavities formation and solar cells processing are described in Fig. 1.

2.3. Characterization set-ups

Scanning Electron Microscope (**SEM, HITACHI 4800**) was employed for the morphology study. The reflectivity of samples after each processing step was measured by **LAMBDA 950 de Perkin Elmer** UV/Vis/NIR Spectrophotometer equipped with an integrating sphere in the 300–1100 nm wavelength range. The FTIR spectra were recorded using **Nicolet MAGNA-IR 560** Spectrometer with a resolution of 2 cm^{-1}. The variation of the effective minority carrier lifetime was evaluated using **Sinton WCT-120 Lifetime tester**.

3. Results and discussion

3.1. Etched Si surface morphologies

3.1.1. Kinetic reaction

Fig. 2 shows SEM images of Si substrates before and after Ag-ACVE. The isotropic etching in CP_4 acid solution leads to a clean substrate with a flat and smooth surface (Fig. 2(a)). After dipping in $HF/AgNO_3$ aqueous solution during 1 min (Fig. 2(b)), the sample is covered with a silver dendritic structure. Indeed, the $AgNO_3$ metallic salt dissociates in the HF aqueous solution to give metal ions Ag^+. The Ag^+ ions coming in contact with the Si substrate extract electrons and are reduced into metallic nuclei then growth to nano-clusters and isolated nanoparticles or continuous layer. The electroless deposition of Ag occurs according to the following cathodic reaction (1):

Table 1
Detailed summary of Si etching condition.

Sample name	A_5	A_{20}	A_{40}	A_{60}	A_{80}	A_{100}	B_0	B_{10}	B_{30}	B_{50}	B_{70}	B_{90}
Etching duration (min)	5	20	40	60	80	100	60	60	60	60	60	60
molar ratio $\rho_{H_2O_2}$(%)	90	90	90	90	90	90	0	10	30	50	70	90

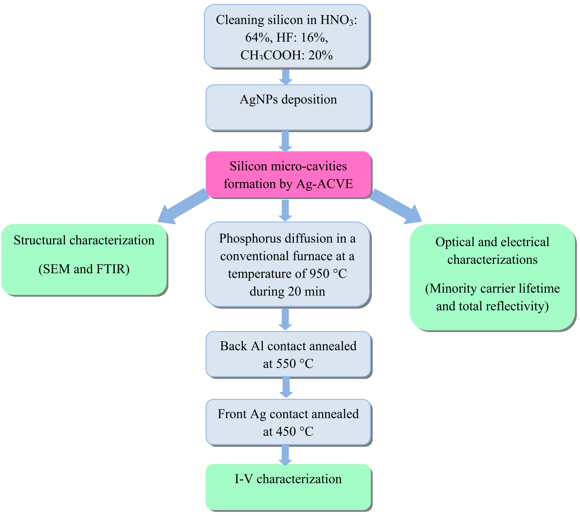

Fig. 1. Flow chart of Si micro-cavities formation and solar cells processing.

$$Ag^+ + e^- \rightarrow Ag \qquad E_{Ag}0.78V \quad vs. \quad SHE \tag{1}$$

However, the detailed mechanism of the metallic dendritic structure is still under debate due to the difficulty in in-situ exploration of the growth of process. Ouertani et al. [17] explain that the evolution of the silver structure from nanoparticles or nanoclusters to a dendritic pattern is related to Ag^+ concentration and dipping duration.

In the second step and in order to study the reaction kinetic of Ag-ACVE, the Ag-loaded Si substrates are submitted to an acid vapor emanating from HF/H_2O_2 hot solution at different durations 5, 20, 40, 60, 80 and 100 min and a fixed molar ratio $\rho_{H_2O_2}$=90%. For short etching duration (5 min), the surface morphology of the sample A_5 (Fig. 2c) presents an un-homogeneous grooved surface with low density of micro-cavities with diameters less than 2 µm. This un-homogeneous is mainly due to the short etching duration inducing the condensation of a quite un-sufficient HF/H_2O_2 quantity leading to isolated etching sites. When the etching duration reaches 20 min (Fig. 2d), the entire surface of the sample A_{20} should be pervaded by the condensed vapors. So that, a spongy like-microstructure is distributed on the whole surface with a fractal distribution of micro-cavities. This spongy structure is mainly due to the gradient of the reactant concentration resulting from an outstanding chaotic adsorption of the reactant molecules on the top surface. Fig. 2(e) and (f) reveal that increasing etching duration from 20 to 60 min leads to the widening of the micro-cavities diameter from 3 to 20 µm without affecting the spongy structure. The various linear grooving in perpendicular and parallel to the Si surface is due to the isotropic travelling of the AgNPs as a result of the chaotic vapor interaction with the catalyst.

Similarly to the other vapor phase etching mechanism [18,19], the formation of Si micro-structures during the Ag-ACVE requires a preliminary regime called “incubation regime”. During this regime the vapors acids condense on the AgNP coated surface until they agglomerate together forming acid droplets than a continuous aqueous acid layer. At this stage, etch H_2O_2 molecule is reduced at the AgNPs surface consuming protons (H^+) provided by the acid electrolyte medium and generating two holes (h^+) according to the following cathodic reaction (2):