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Research Article
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Correlation Between Oxidant Concentration and Morphological Properties of Silicon Nanowires Obtained by Silver-Assist Electroless Etching

Besma Moumni* and Abdelkader Ben Jaballah

Laboratory of Photovoltaic, Research and Technology Centre of Energy, Borj Cedria Technopark, BP 95, Hammam-Lif 2050, Tunisia

Abstract

In this work, a correlation between oxidant concentration and the morphological changes of silicon nanowires formed by a two-step silver-assist electroless etching method is established. It reveals that a textured silicon surface appears for samples etched at relatively H_2O_2 concentration lower than 2%. However, The dynamic and kinetics of silicon nanowires for different H_2O_2 concentration (5%, 7% and 8%) are studied by scanning electron microscopy. We found that the thickness of etched silicon nanowires as a function of time fallows a linear law. The length of silicon nanowires is not only H_2O_2 concentration dependent but a critical is necessary to overcome length saturation. We prove also that the oxidation rate of silicon facing Ag particles can limit the dynamic of wire formation, due to the generation of silicon hexafluoride ion $(SiF_6)^{2-}$.

Keywords: Silver nanoparticles; Silicon nanowires; H_2O_2 concentration

Introduction

Beside ten years ago, silicon nanowires (SiNWs) have attracted wide interest because of their capability to be implemented as an active material for energy conversion and storage. Photovoltaic devices [1-4], supercapacitors and lithium batteries [5] that can be used for power management are fabricated and tested in silicon nanowires based technology. Fabrication of SiNWs with controlled diameter, length, and electronic properties are essential to these applications. Indeed, significant progress has been made in the development of facile and controlled methods for SiNW fabrication. For instance, SiNWs have been prepared by various methods comprising Vapor-Liquid-Solid (VLS) growth [6,7], and Metal-Assist Chemical Etching (MACE) which is the prominent procedure [8,9] used in plane solid-liquid-solid mechanism [8]. To become cost-effective, a simple and cheap process is needed to synthesize the silicon nanowires. In this work, silicon nanowire arrays are obtained from solar grade silicon for the first time by Ag-assisted electroless etching of Si in solution containing hydrofluoric acid and different concentration of water peroxide (HF/H_2O_2). The morphological and dynamics of wire formation involving the effect of the reactants concentrations and the etching time are studied by Electron Scanning Microscopy (SEM) technique. The prepared arrays of SiNWs can be implemented in many applications such as, photovoltaics, lithium batteries, gas sensors as well as photonic devices.

Experimental

The silicon samples used in this work is p-type, boron doped, the resistivity 7 Ω.cm, thickness 450 µm and (100) oriented. These samples of surface 2 × 2 cm^2, successively degreased in boiling in solution from acetone and ethanol for 5 min. The production process simply comprised three steps. Preliminary, wafer pieces are cleaned following the RCA1 or RCA2 process. After that, silver nanoparticles are scratched onto the Si surface from 10% HF and 0.02 M $AgNO_3$ solution. Finally, the Ag nanoparticles-covered Si wafers are immersed into 10% HF while the H_2O_2 concentrations vary from 3% to 8%. The etching times are, 30, 120, and 241 min, respectively. Next, after formation of black surface, samples are immersed in 50% concentration nitric acid solution for remove the silver particles, finally, rinsed in ionized water and dried under nitrogen flux at room temperature. The correction between H_2O_2 concentration, the morphology and the kinetic formation of SiNWs are explored by Scanning Electron Microscopy.

Results and Discussion

Figure 1 depicts the formation of silver nanoparticles at the surface of planar silicon in aqueous 10% HF and 0.02 M $AgNO_3$ solution. They are formed through an oxido-reduction reaction. This electrochemical oxidation-reduction process itself can lead to the local dissolution of silicon. The simultaneous reduction of Ag^+ metal ions, as well as oxidation and dissolution of silicon yelds the formation of porous silicon and nanowires in an HF/$AgNO_3$ solution. A subsequent etching in a solution of HF and water peroxide (different concentrations of H_2O_2) at ambient temperature leads to the formation of a textured surface of silicon which propagates in volume of silicon when the time etching increases (Figure 2). The generation of textured silicon surfaces is the key step which initiates the formation of nanowires of different sizes (diameter, length and density). Figure 3, shows scanning electron microscopy surface images of as grown silicon nanowires for different concentration of H_2O_2 for etching time equals four hours. The nanowires are distributed uniformly and vertically to the surface of the substrate. The nanowires obtained with lower concentration of H_2O_2 are isolated from each other. However, tips of the nanowires congregate together and become increasingly rough, when the concentration of H_2O_2 increases as the case of 8% concentration.

Cross section scanning electron microscopy images of the nanowires with different H_2O_2 concentration in Figure 4, show that the length of silicon nanowires is not only H_2O_2 concentration dependent, but also relies on the oxidant concentration. This effect is explained by the fact that the thermodynamic reaction becomes more favorable with the

***Corresponding author:** Besma Moumni, Laboratory of Photovoltaic, Research and Technology Centre of Energy, Borj Cedria Technopark, BP 95, Hammam-Lif 2050, Tunisia, Tel: 0021655459671; E-mail: moumnib_fst@yahoo.fr

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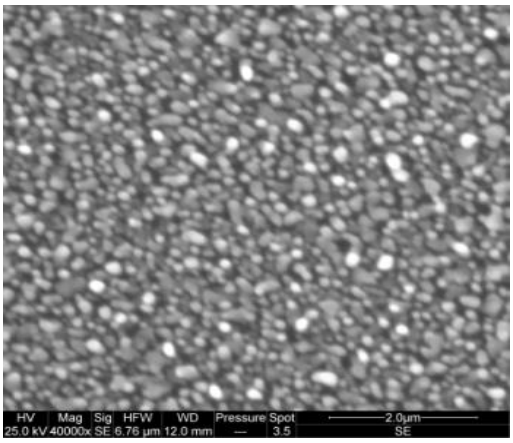

Figure 1: Top views scanning electron microscopy images of silver nanoparticle Formed in a solution of HF/$AgNO_3$.

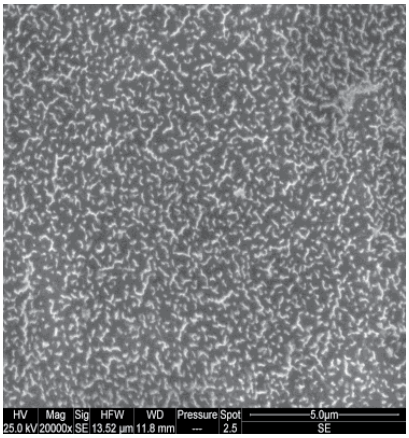

Figure 2: Scanning electron microscopy images of Si substrate after chemical etching in a solution of HF and oxygenated water H_2O_2 revealing the textured structure.

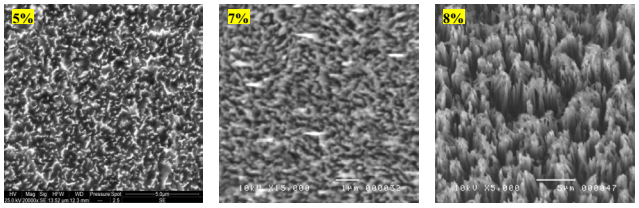

Figure 3: Top views scanning electron microscopy images of the nanowires with different H_2O_2 concentration for an etching duration equals 4 hours.

increase of H_2O_2 concentration due to the of etching potential. Silicon nanowires are formed from this process, silver particle is oxidized by H_2O_2 leads the localize of Ag^+ ion. These silver ion react with silicon and take electrons from silicon near the Ag/Si interface and be recovered into silver particles again. The etching is localized around the silver nanoparticles which are trapped in the nanopits created by themselves. The continued etching in the vertical direction preserve the formation of vertical and aligned silicon nanowire array. In this case, the Ag^+ ions may not be 100% recovered into the silver nanoparticles, with some of which may diffuse out. When the amount of the out-diffused Ag^+ ions reach a certain threshold, these silver ions may start to nucleate on the

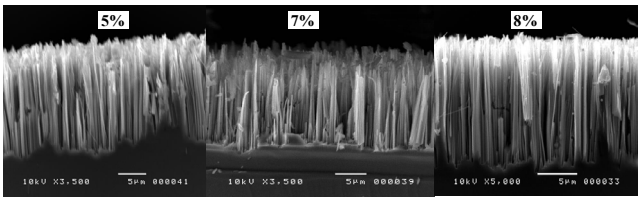

Figure 4: Length and shape variation of the nanowires with different H_2O_2 concentration for an etch duration equals 4 hours.

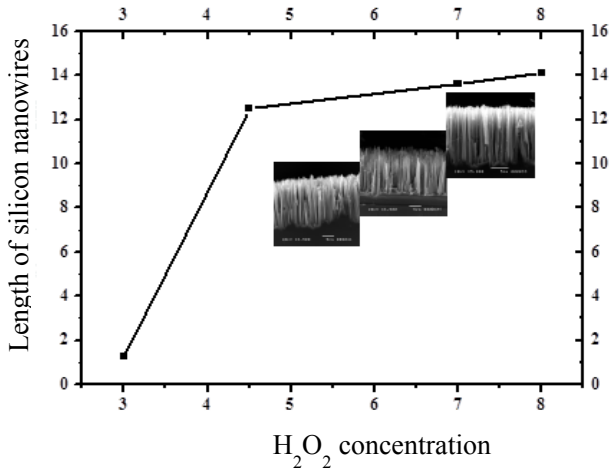

Figure 5: Kinetic growth of silicon nanowires produced by MACE for different H_2O_2 concentration at ambient temperature.

side wall near certain weak defectives sites (e.g., around the dopants) by extracting electrons from the silicon nanowires and forming new silver nanoparticles for a new etching pathway along the lateral direction of the nanowires.

The dynamic and kinetics of wire formation is shown in Figure 5. It reveals a linear dependence: the thickness of etched silicon as a function of time fallows a linear law. The phenomenon is the same for different concentration of H_2O_2 (5%, 7% and 8%). Undoubted, silver nanoparticules play an essential role during the formation of the nanowire structure rather than a catalytic effect initiating the formation of pits. Then, the average speed of Ag in silicon can equalize the chemical etching rate of silicon leading to the nanowire formation. As described above, the formation mechanism is a two step process; oxidation of Si at the anode site and reduction of H_2O_2 (or H^+) at the cathode site would result in a net flux of electrons through the Ag particle, leading to a selective etching of silicon. The oxidation of silicon facing Ag particles can limit the dynamic of wire formation; first due to the resistive effect of silicon and second due to the generation of silicon hexafluoride ion $(SiF_6)^{2-}$ due to the dissolution of silicon oxides.

Conclusion

We conclude that the nanowires etched with lower H_2O_2 concentrations are isolated from each other. However, when the concentration of H_2O_2 increases, the surface of the nanowires becomes rough and the tips of the nanowires congregate together. Three different behaviors of H_2O_2 are claimed based on kinetic growth of the silicon nanowires revealed by scanning electron microscopy showing that the water peroxide concentration is a key feature for the formation of deep nanowires at the surface of silicon.

Authors' Contributions

Moumni Besma: Experimental sample and Writing paper. Ben Jaballah Abdelkader: Interpret results.

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