Effect of the experimental parameters on the shape and formation kinetics of SiNWs formed by electroless chemical etching in aqueous $AgNO_3/HF/H_2O_2$ solution

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The discovery at the beginning of 1990 of carbon nanotubes awaked the interest for one-dimensional (1D) nanostructures. Currently, silicon nanowires (SiNWs) formed by electroless chemical etching in aqueous $AgNO_3/HF/H_2O_2$ solution, arouse great interest due to their physical properties and potential applications. The understanding of physical-chemical phenomena that occur during the formation of SiNWs, the effect of etching parameters on their morphology, the formation mechanism and formation kinetic raise many questions. In this paper, we investigate the effect of etching parameters; namely $AgNO_3$ concentration, HF concentration, etching time and the volume of H_2O_2 on the shape of obtained nanostructures. The formation kinetic was investigated by studying the effect of the etching time on the morphology of obtained nanostructures. SiNWs studied in this work were formed on a P type and (100) oriented monocrystalline silicon substrate. Characterization of formed SiNWs was performed using a scanning electron microscope (SEM).

1 Introduction

Metal-assisted electroless etching is one of top-down approaches that allow forming silicon nanostrures on silicon wafer [1-3]. Depending on experimental parameters, porous Si with different morphologies, nanowires (SiNWs) as well as nanoholes of different shapes can be produced [1-4]. As a consequence of the geometrical dependence of physical and electrical properties of SiNWs based devices, it is very important to fabricate SiNWs in a well-controlled manner [5]. Hence, the study of the effect of electroless etching parameters on the shape of SiNWs becomes very interesting.

In this paper, we investigated the effect of the experimental parameters on the shape of silicon nanostructures fabricated by electroless chemical etching in aqueous $AgNO_3/HF/H_2O_2$ solution. The morphology of etched layers formed on silicon was investigated by a scaning electron microscope (SEM).

2 Experimental process

SiNWs are prepared by silver assisted chemical etching in HF aqueous solution [6-8]. We used boron-doped monocrystalline silicon, (100) oriented, with a thickness of 200 µm and a resistivity of 0.5-3.0 Ωcm. For the samples cleaning, we immerse them in a boiling acetone for 10 min and then in ethanol for 5 min to remove organic greases. After rinsing three times with de-ionized water (DIW), samples are etched in a 5% aqueous HF solution during 2 min to eliminate native silicon dioxides. After cleaning samples were immersed into the etching solution containing $AgNO_3$ solution, 10 ml aqueous HF solution and H_2O_2 at room temperature. After etching, to remove the silver film, we immerse samples in HNO_3 (44%) aqueous solution for several minutes.

3 Results: Effect of experimental parameters

3.1 Cleaning protocol

During etching, we remark that the cleaning step of Si samples influences the morphology of obtained nanostructures. In Fig. 1, we give top SEM images performed on three samples. In Fig. 1(a), the sample was immersed in acetone during 5 min and in ethanol during 5 min. Then we immerse it in a sulfuric acid-hydrogen peroxide mixture H_2SO_4 (97 %):H_2O_2 (30%) with a volume proportion 3:1 for 10 min. After that, the sample is rinsed with ultra-pure water, followed by a dipping in 5 % HF for 1 min and finally rinsed with ultra-pure water. A second sample, which is imaged in Fig. 1(b), was immersed in a hydrochloric acid- hydrogen peroxide mixture HCl (40%):H_2O_2 (30%) with a volume proportion 1:1 for 8 min. Then, the sample was rinsed with ultra-pure water, and finally in acetone and isopropanol during 10 min each. The third sample (Fig. 1(c))) was immersed in a boiling acetone for 10 min then in ethanol for 5 min. After this step, the sample was rinsed three times with DIW. Finally, the sample was etched in a 5% aqueous HF solution for 2 min to eliminate native silicon dioxide. All three samples were etched in a 40% HF aqueous mixed with a 0.02 M $AgNO_3$ aqueous solution for 60 minutes at ambient temperature. Regarding SEM images of Fig. 1, one can notice that we obtain a porous like structure for sample corresponding to Fig. 1(a), however, for those of images (b) and (c), we obtain SiNWs. In addition, we notice that SiNWs in Fig. 1(b) are homogeneous as compared to those obtained for the third sample (Fig. 1(c)). The latter difference in homogeneity is attributed to the role of HCl:H_2O_2 in homogenizing the thickness of the oxide layer, leading to a uniform etching of Si [9]. Obtained results confirm the effect of the pre-surface treatment on the morphology of silicon nanostructures obtained by Shiu et al. [10].

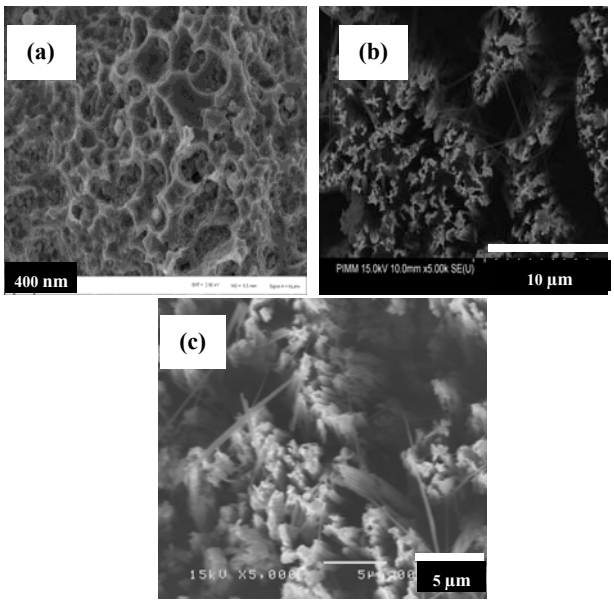

Figure 1 Top surface of the SEM image of silicon nnanostructures vs. cleaning protocol.

3.2 Etching time

As compared to other etching processes, formation of SiNWs has a particular kinetic. The latter was investigated by studying the effect of the etching time on the morphology of obtained silicon nanostructures. In Fig. 2, we give SEM images of formed SiNWs fabricated during 10, 20, 30, 40, 50 and 60 minutes in an etching solution mixed with a 10 ml $AgNO_3$ solution (0.050 M), 10 ml aqueous HF solution (40%) and 1 ml H_2O_2 (10.00 M). In each top surface SEM image, we give in the upper right inset its cross-sectional SEM view. All top SEM images used in Fig. 2 were performed at the same magnification (x 10 000). We notice that SiNWs are formed uniformly. Cross-section images show that for short durations, SiNWs are not uniform.

Using top SEM images of Fig. 2, we estimate values of the porosity by performing a fine mesh; Porosity is defined as the ratio of vacant cells by the total number of cells. In Fig. 3(a), we plot the shape of the porosity profile vs. etching time. Values of porosity vary in a relatively medium domain: from 33 % to 68%. From cross-sectional SEM images of Fig. 2, we measured the length of SiNWs, which we give in Fig. 3(b) as a function of the etching duration. As clearly seen in the cross-sectional SEM images of Fig. 2, the length of SiNWs is not homogeneous, for this reason we took three different values of length of nanowires, black dots correspond to the length of the shortest nanowire, red dots correspond to the length of the average nanowire and green dots correspond to the length of the longest nanowires. Length of obtained SiNWs is plotted with error bars, where mean values vary from 11.5 µm to 25.8 µm. We notice that the length of SiNWs increases as the etching duration increases, according to the schemed curve shown with a blue line, which deviates slightly from the linear shape as obtained in references [5] and [11].

In Fig. 3(c), we plot the etching rate of Si vs. the etching time. We note that the etching rate decreases as the etching time increases. The etching rate was defined as the ratio of the SiNWs length by the etching time.

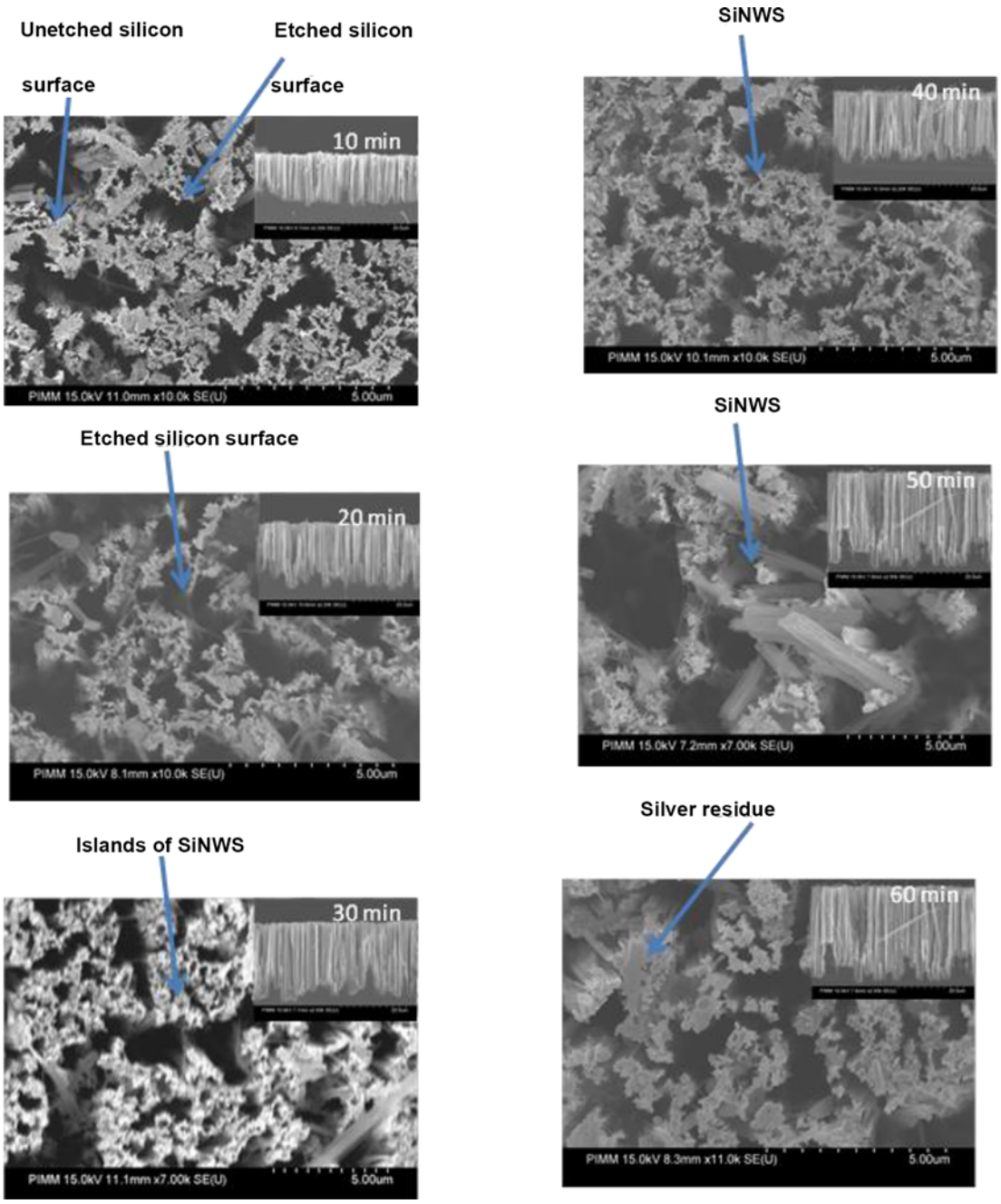

Figure 2 Top surface of the SEM images of SiNWs vs. etching time.

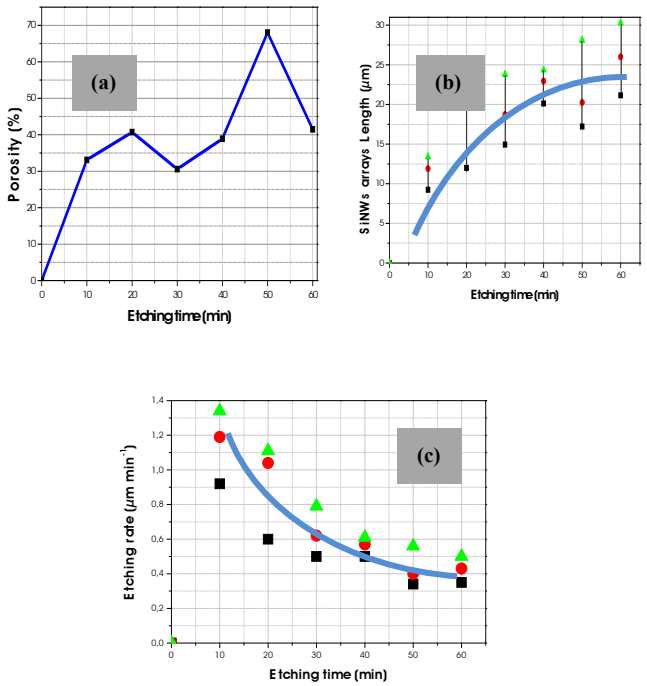

Figure 3 Porosity (a), length (b) and etching rate (c) of SiNWs vs. etching time. In (b) and (c), the blue lines were used to show the dependencies vs. etching time.

3.3 $AgNO_3$ concentration

In this section, we discuss the effect of $AgNO_3$ concentration on the surface morphology of obtained SiNWs. Samples were etched in the $AgNO_3$/HF (40%) solutions with 1 ml (10 M) H_2O_2, for 60 min. $AgNO_3$ concentration was varied from 0.010 to 0.050 mol/l.

After removing the silver films in nitric acid aqueous solution for several minutes, and rinsing samples with DIW, samples undergoe SEM investigation. In Fig. 4 we give the top SEM images of prepared samples, and, in Fig. 5, we give their cross-sectional SEM images. All top SEM views were performed at the same magnification (×2 000). Used $AgNO_3$ concentrations are M = 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045 and 0.050 mol/l.

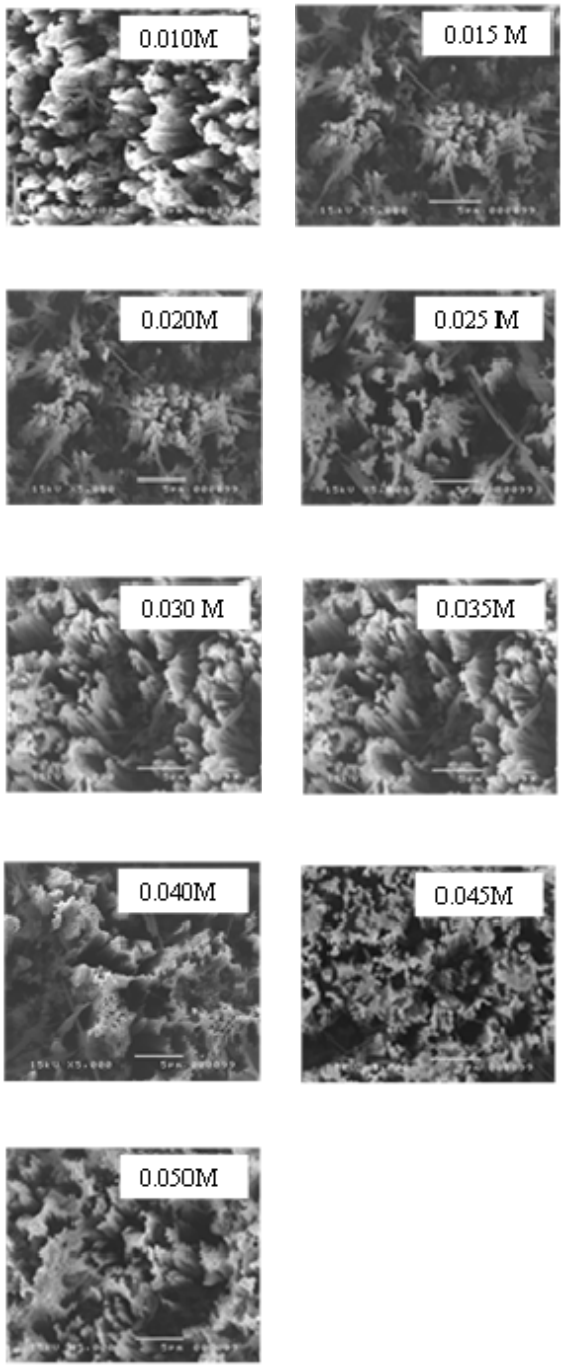

Figure 4 Top surface SEM images of silicon nanostructures vs. $AgNO_3$ concentration.

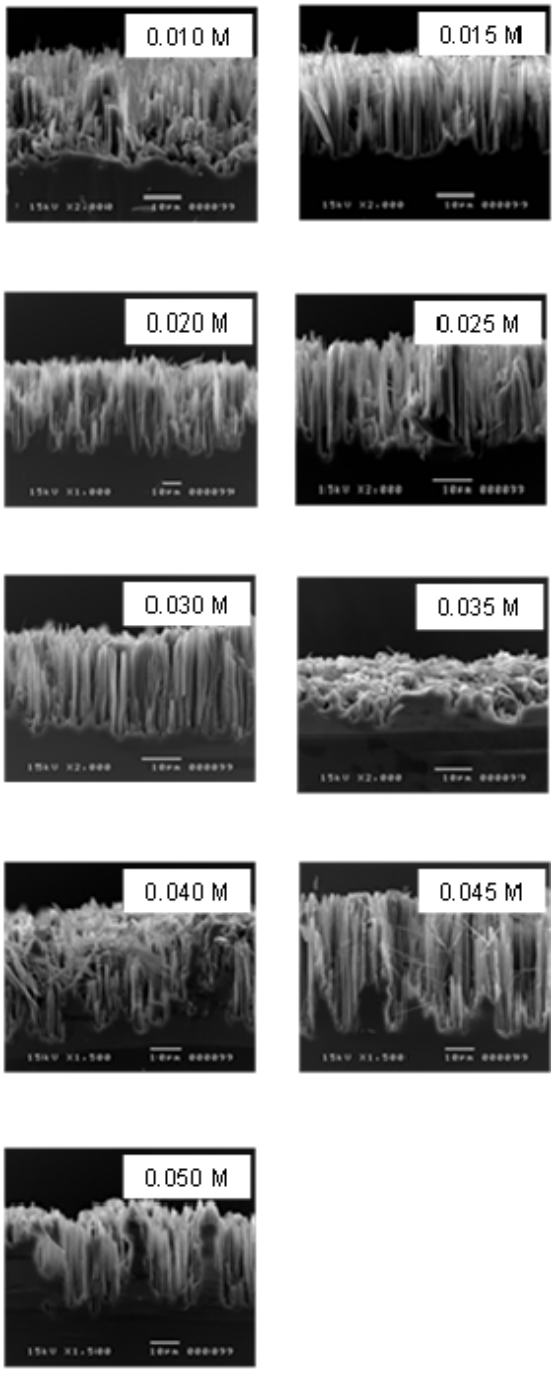

Figure 5 Cross-sectional SEM images of SiNWs vs. $AgNO_3$ concentration.

According to the obtained SEM images, we obtain SiNWs for all concentrations. However, different shapes of the formed films can be observed. Hence, for samples etched with $AgNO_3$ concentrations; M=0.010; 0.025, 0.035, 0.040, 0.045 and 0.050 mol/l solutions, SiNWs are not homogenous. However, wires are well organized when formed with an $AgNO_3$ solution at concentrations 0.015, 0.020 and 0.030 mol/l.

Using SEM images of Fig. 5, we plot in Fig. 6 the variation of the length of SiNWs vs. used $AgNO_3$ concentrations. Variation of the SiNWs length has an alternative behavior between formation and dissolution of wires. Hence, we obtain two intervals of $AgNO_3$ concentrations for which the SiNWs formation starts, and tow intervals for which the dissolution of wires begins. In addition, we obtained values of the $AgNO_3$ concentrations for which the rate of SiNWs dissolution is very high.

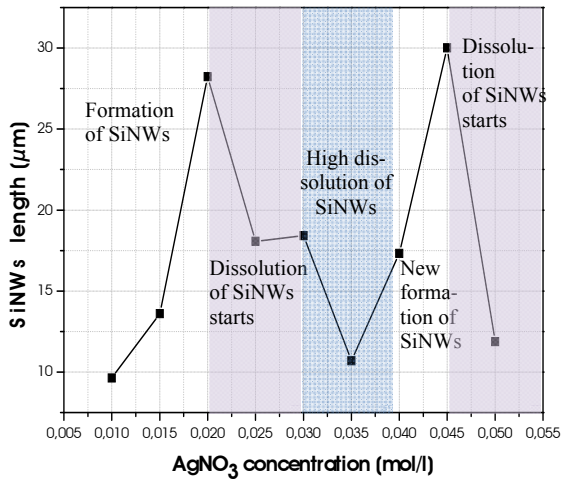

Figure 6 Length of obtained SiNWs vs. $AgNO_3$ concentration (in mol/l).

3.4 HF concentration

To study the effect of the HF concentration on the morphology of obtained Si nanostructures, we etched Si samples in three HF aqueous solution; 10, 20 and 40%. Samples in this experiment were cleaned as follows: immersion in a hydrochloric acid- hydrogen peroxide mixture HCl (40%): H_2O_2 (30%) at a volume proportion 1:1 for 8 min, then, they are rinsed with ultra-pure water, and finally immersed first in acetone and second in isopropanol during 10 min for each immersion.

After cleaning, silicon samples are immersed in a 10 ml aqueous $AgNO_3$ solution (0.020 M) mixed with 10 ml aqueous HF solution at different concentrations, for 60 min. After etching, the silver film was removed using a diluted HNO_3 (44%) aqueous solution for several minutes.

When the etching was processed in 10% HF solution, we obtain a pore formation on the Si sample as observed in Fig. 7. When HF concentration is increased to 20%, the density of the formed pores increases as observed in the middle image of Fig. 7. However, with a 40% HF etching solution, we obtained SiNWs.

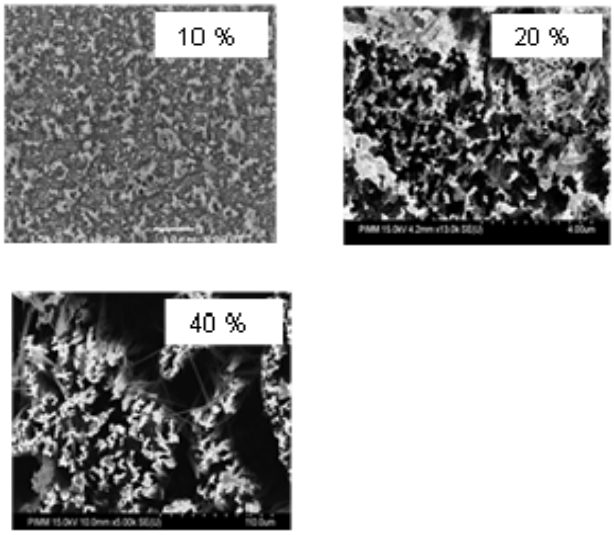

Figure 7 Top surface SEM images of Si nanostructures vs. HF concentration.

3.5 H_2O_2 volume

In order to clarify the effect of the H_2O_2 oxidant agent on the etching rate of silicon, two samples of (100) p-type Si of resistivity 1-2 Ω cm were etched in 10 ml aqueous $AgNO_3$ solution (0.02 M), 10 ml aqueous HF solution (40%) and two different volumes of H_2O_2 (30%). The etching duration is 30 minutes.

The left SEM image of Fig. 8 corresponds to a Si sample etched without additional oxidant ($V(H_2O_2)$=0 ml). This image shows a formation of a superficial porous layer with an estimated thickness of about 1 µm at maximum. When we add 10 ml of a H_2O_2 solution, we obtain a macrospores structure as shown in the right SEM image. The thickness of the formed layer is about 11 µm. The latter value was determined from the cross-section SEM view of this sample as given in the top right side of the corresponding image. Using these thicknesses, we assess that for both cases; without and with H_2O_2, the etching rate is 0.05 and 0.36 µm min^{-1}, respectively. Obtained values of the etching rate are in accordance with the result obtained by authors of Ref. [12].

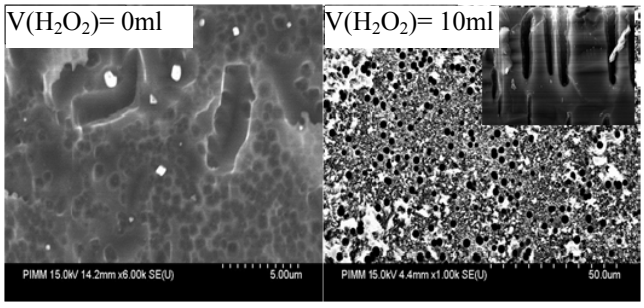

Figure 8 SEM images of silicon nanostructures vs. H_2O_2 volume.

4 Conclusion

In this work, we give results related to the effect of different experimental parameters influencing the shape and the kinetic formation of silicon nanostructures. Hence, we studied the effect of the cleaning protocol, the etching duration and the etchant concentration on the morphology of etched silicon layer. We pointed out that the morphology strongly depends on the etching parameters. We found that the pre-surface treatment influences the morphology of obtained silicon nanostructures. Under suitable experimental conditions leading to the formation of SiNWs, we remark that the length of these wires increases when the time etching was increaed. When we vary the $AgNO_3$ concentration, we obtain two intervals of $AgNO_3$ concentrations for which the SiNWs formation starts, and tow intervals for which the dissolution of wires begins. In addition, we obtained values of the $AgNO_3$ concentrations for which the rate of SiNWs dissolution is very high. For the variation of HF concentration, no nanowires are formed at HF concentration lower than 40%. For the effect of H_2O_2, we found that when we add this oxidant agent to the etching solution, the etching rate of silicon increases considerably.

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