Silicon Nano-Pillars on Silicon Substrate by Metal-Assisted Chemical Etching (MACE)

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ABSTRACT

This paper investigates the use of metal-assisted chemical etching (MACE) to synthesize nanostructured Si substrates. The aim is to produce uniform Si nano-pillars and determine their growth profile. To achieve this, a two-step MACE process was applied. The process involved a two-step MACE approach, with each sample deposited in HF/$AgNo_3$ solutions for 4 min and etched in etching solutions (HF/H2O2) for 45 minutes using specific concentrations in solution which are 0.02M, 5M, and 0.35M for Ag, HF and $H_2 0_2$ respectively and 1000 ml of distilled water in between each process. Notably, solutions containing HF were prepared in Teflon containers, while the rest of the processing was carried out in Pyrex containers. The results of the study showed the formation of Ag nanoparticles and uniform Si nanopillars, as observed through SEM readings, which indicated the same pillar size of 0.70 µm and a separation of 0.84 µm at every measured nanopillar. Based on these findings, it can be inferred that MACE is a viable technique for synthesizing nanostructured materials.

Keywords: Nanostructured, metal-assisted chemical etching, nano-pillar, etching process, MACE.

1. INTRODUCTION

Metal-assisted chemical etching (MACE) is a technique used to create silicon nanostructures with high aspect ratios. It is considered a promising approach for preparing nanostructures that are difficult to produce using other conventional methods [1]. Compared to other techniques such as vapor-liquid-solid growth, reactive ion etching, and electrochemical etching, metal-assisted chemical etching is more versatile and effective, which makes it a popular choice for creating silicon nanostructures [2].

Wet etch processes, like the one described here, are generally considered more cost-effective and simpler to implement compared to dry-etching approaches. As reported by Romano *et al*. (2020) [3] MACE is a process that can achieve significantly higher aspect ratios than most other etching processes.

According to Huang *et al*. [3] the metal-assisted chemical etching method is widely used these days, but it was first studied in detail by Li and Bohn. They found that when a thin layer of noble metal, such as Au, Pt, or Au/Pd alloy, was sprayed onto the surface of a Si substrate, it catalyzed the etching of Si in a mixed solution containing HF, H_2O_2, and EtOH. This resulted in the formation of straight pores or columnar structures.

Although the process of metal-assisted chemical etching is a reliable method for creating Si nanopillars, it only works for inorganic semiconductors like silicon and gallium. To achieve consistent results, it's crucial to control the etchant concentration carefully. It's also important to note that the process involves using highly hazardous materials such as concentrated hydrofluoric acid, so appropriate safety precautions are necessary [4].

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Thus, the aim of this study is to determine the reaction mechanism involved in the creation of Si nanopillars. This process involves two steps. First, the substrate is synthesized through metal-assisted chemical etching, using 0.02M of silver (Ag), 5M of hydrofluoric acid (HF), and 0.35M of hydrogen peroxide (H_2O_2). Second, the morphology of the nanopillars is examined through SEM imaging.

2. EXPERIMENTAL PROCEDURE

A nanostructured silicon with a 3cm x 3cm dimension was synthesized using the metal-assisted chemical etching (MACE) technique on p-type, <100>, 0-10 ohm. The Silicon wafer was immersed into a solution of undiluted hydrofluoric acid (49%) and nitric acid (69%) with a volume ratio HF: HNO_3 of 1:100 for 10 minutes then was immersed into HF: H_2O with a ratio 1 to 50. Subsequently, the wafer was dipped into 10% sodium hydroxide (NaOH) at 80°C for 30, soaked into HF: H_2O, followed by rinsing with distilled water to ensure the wafer was hydrophobic.

After that, silver nitrate ($AgNO_3$) was used as a depositor to form a randomly distributed matrix of Ag nanoparticles on the Si wafer in HF/$AgNO_3$ solution for 4 minutes continuously by washing the wafer into HF/H_2O_2 for 45 minutes. Next, it was rinsed immediately with distilled water then it was soaked in HNO_3 for 5 minutes for Ag removal. The synthesis of nanostructured Si substrates using the metal-assisted chemical etching (MACE) method will be conducted based on a previous study by A.W Azhari *et al*. [5].

All etching experiments have been performed based on optimization as stated in Table 1 and the concentration as stated in Table 2 while Table 3 shows the parameter used in this experiment and the process flow for this experiment is shown in Figure 1.

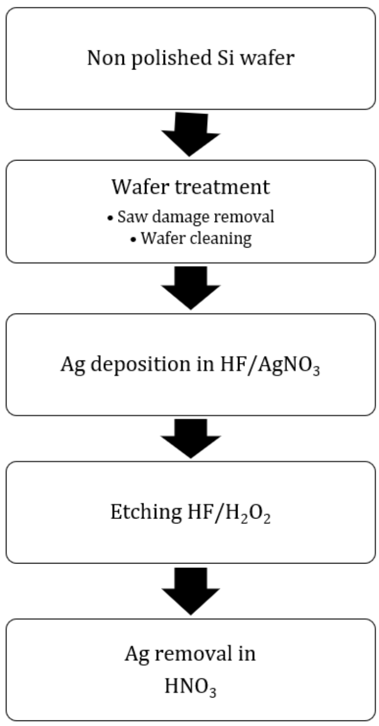

Figure 1. The process flow involves in two-step MACE process

Table 1 The optimization from a previous study by Azhari *et al.*[5]

Constraints	Goals
Ag concentration	Minimized
HF concentration (M)	5
H_2O_2 concentration (M)	0.1-0.5
Deposition time (min)	1 – 5

Table 2 The concentration parameter for deposition solutions with factors

Stages	Factors	Factors		
		Low	Med	High
Deposition	Ag Concentration (M)	0.01	0.03	0.05
	HF Concentration (M)	4	7	10
	Time (min)	1	5.5	10
	Temperature	Room temperature (35°C)		

Table 3 Parameter used in this experiment

Parameter	Level
Ag concentration (M)	0.02
HF concentration (M)	5
H_2O_2 concentration (M)	0.1-0.35
Deposition time (min)	45
Etching time (min)	32-58

3. RESULTS AND DISCUSSION

Figure 2 (a) shows the plan view of the samples that are being deposited in HF/$AgNO_3$ for 4 minutes. Upon close examination, it is evident that the deposition of Ag particles is taking place. The SEM image of the deposited Ag in Figure 2(a) unambiguously displays white spots all over the silicon surface. This provides evidence that these white spots are, in fact, Ag nanoparticles that are randomly distributed on the silicon surface, as previously stated in a well-established research study [6].

In Figure 2(b) The porosity of a silicon wafer was evidenced by the presence of small holes on its surface. The morphological changes of a silver-coated silicon wafer in an aqueous solution of hydrofluoric acid were also observed containing oxidizing nitrate as mentioned in by previous study by Hu *et al.* [7] as well as suggested that the etch rate of HF is always higher than its formation rate by H_2O_2, excessive local silicon oxidation and dissolution occur, resulting in microroughness or pitting of the silicon surface owing to irregular etching.

Figure 2(c), shows the sample is separated and the etched poly-Si due to a proper drying technique as mentioned by Huo *et al.* [1] where during the production of high-aspect-ratio vertical nanowires, the process of supercritical drying plays a critical role. This process involves drying the nanowires using supercritical fluids, which results in the separation of domain boundaries. These boundaries are believed to be of the same size as a single Si crystallite, which is essential for the proper functioning of the nanowires. This separation allows the nanowires to maintain their vertical orientation, which is crucial for their performance and efficiency.

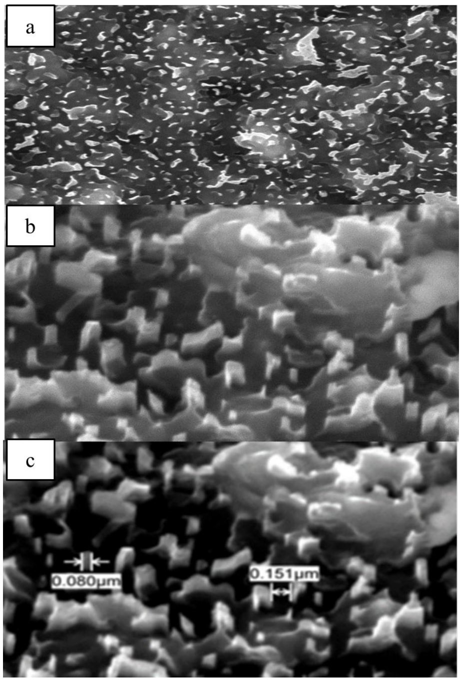

Figure 2. Result of deposition of Ag particles where (a) display a white spot all over the Si surface (b) presence the porosity of a Si wafer and (c) display a sample is separated and etched after being deposited in Ag/NO3 after 4 minutes.

MACE process after being etched for 45 minutes. Figure 3(a) upon examining the SEM image in plan-view, it becomes apparent that the samples have clustered together, forming a distinct pattern. Despite this clustering, it is can still observe the presence of pillars within the sample. Figure 3(b) at a point view of 30°, the SEM image clearly depicts the presence of formed and positioned nanopillars.

This observation serves as a testament to the effectiveness of the MACE process in creating the desired microstructure on the substrate. As indicated in flowchart 1, the final step in MACE is to remove Ag the in HNO_3 solution. In his study, Daoudi *et al.* (2020) mentioned that the use of silver to assist the etching of Si in the present experiments could result in partial dissolution of the silver by the etching solution. As a result, during the etching process, the silver gradually dissolves, and the diameter of the holes on the silver film gradually increases, creating nano-pillars [2].

Figures 3(c) and (d) show a growth profile of the Si nano-pillars hence, also assist in the formation of uniform Si nano-pillars. In Figure 3(c) shows the same pillar size from two pillar sizes of 0.70 µm. While in Figure 3(d) shows a separation of 0.84 µm at every nanopillar that has been measured.

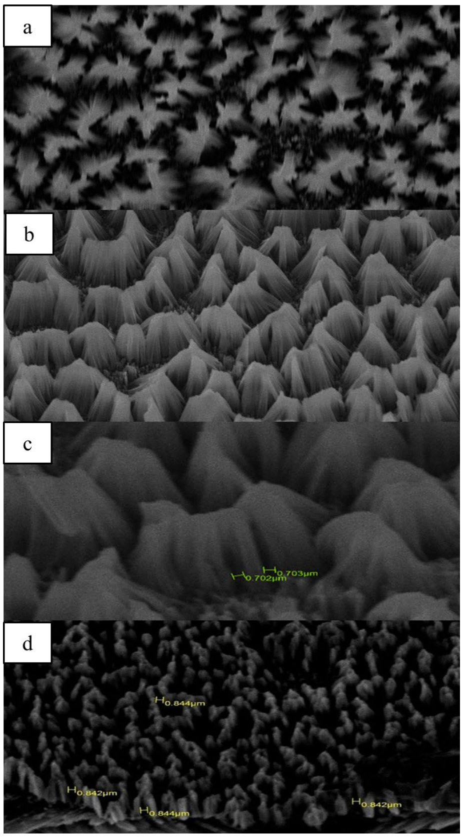

Figure 3. Result of MACE after 45 minutes. (a) showing a SEM image in plan view (b) at 30°-point view, showing the formed and positioned nano-pillars (c) showed a growth profile of Si nano-pillar and (d) showed a uniform separation of nano-pillars.

4. CONCLUSION

From this we have obtained results of the study showed the formation of Ag nanoparticles and uniform Si nanopillars, as observed through SEM readings, which indicated the same pillar size of 0.70 µm and a separation of 0.84 µm at every measured nanopillar which resulted from the deposited in HF/$AgNo_3$ solutions for 4 min and etched in etching solutions (HF/H_2O_2) for 45 minutes using specific concentrations in solution which are 0.02M, 5M, and 0.35M for Ag, HF and H_20_2 respectively and 1000 ml of distilled water in between each process. This can be concluded that this research effort will help establish the role of two-step metal-assisted chemical etching in low-budget and also show the formation of Ag nanoparticles and as well as obtained uniform Si nanopillars as observed through SEM readings.

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