**Synthesis of Silicon Nanowires by Selective Etching Process**

In this paper, selective etching process is used to synthesize SiNWs. This method arises from electroless metal deposition on a silicon wafer through selective etching. The electroless plating technique has many advantages such as low temperature processing and simple process with non-expensive deposition facilities. A clean p-type silicon wafer was etched in an aqueous solution containing hydrofluoric acid (HF) and silver nitrate ($\text{AgNO}_3$) at 60°C for 60 minutes. This aqueous solution was prepared by mixing both HF and $\text{AgNO}_3$ in a plastic beaker and was heated in hot water bath. Electroless silver deposition will take place on the surface of Si wafer and their growth mechanism are analyzed on the basis of a self assembled localized microscopic electrochemical cell model. The structure of SiNWs is observed by using field emission scanning electron microscope (FESEM). It has revealed the formation of SiNWs with diameter ranging from 40 nm to 200 nm with the length of about 20 μm. The unique features of SiNWs have made them potentially applicable in solar cell, chemical sensing devices and basic components for nanoelectronic and optoelectronic devices.

**Keywords:** Silicon nanowires, Etching process, Silicon structures, CVD, PCVD

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**1. Introduction**

Silicon nanowires (SiNWs) are one-dimensional nanostructure which have better feature compared to other low dimensional systems. SiNWs have two quantum confined directions while still leaving one unconfined direction for electrical conduction. Therefore, SiNWs are best used in applications where electrical conduction takes place. The small diameter of these NWs causes them to exhibit significantly different optical, electrical, chemical and magnetic properties from their bulk 3D crystalline materials. Various methods had been successfully used to synthesize SiNWs such as Chemical Vapor Deposition (CVD), Plasma Enhanced CVD (PECVD), Laser-Ablation and Evaporation. However, these methods involve high cost, high temperature, complicated equipments and other rigorous condition. Nanotechnology is expected to have an impact on nearly every industry. The U.S. National Science Foundation has predicted that the global market for nanotechnologies will reach $1 trillion or more within 20 years [1]. Many researches had been done in nanomaterials, nanoelectronics, and bionanotechnology throughout the years. Various methods to synthesize nanomaterials such as nanoparticles, nanowires, nanotubes, nanocomposites and nanostructured had been actively employed. Nanodevices and nanoelectronics have applications in medical treatments and diagnostics, faster computers, and in sensors.

It is reported that, upon exposure to ammonia gas and water vapor, the electrical resistance of HF-etched SiNWs is lower at room temperature compared to non-etched SiNWs. This phenomenon serves as the basis for a new kind of sensor based on SiNWs. The sensor is made by a bundle of etched SiNWs and exhibits fast response, high sensitivity and reversibility [2]. SiNWs can also be used to make diagnostic tools that are based on nanotechnology. These sensor devices can detect diseases in a person and give result within minutes [3]. In addition, SiNWs had been reported to have application in photodetectors and solar cells due to their tunable feature size and large surface area to enhance infrared response [4].

SiNWs are one dimensional and its small diameter had caused them to exhibit unique properties such as good electronic, optical, chemical and magnetic properties and will be a promising candidate for applications in nanodevices compared to bulk 3D material. SiNWs have two quantum confined directions while still leaving one unconfined direction for electrical conduction and therefore it is very conductive.

Throughout the years many effort have been made to improve the synthesis of SiNWs and these includes thermal chemical vapor deposition using SiH₄ gas at 650°C in a flow mixture of H₂.
and N₂ [5]. Besides that, Plasma Enhanced CVD (PECVD), Laser-Ablation [6] and Evaporation method [7] had also been employed to synthesize SiNWs. However, these synthesis techniques are tedious and troublesome and had always involved high cost, high temperature, complicated equipments and other rigorous condition.

In this paper, a simpler and cheaper method had been employed. This method involved electroless metal-particle-assisted etching [8]. Electroless metal deposition in ionic metal (silver) HF solution is based on micro-electrochemical redox reaction in which both anodic and cathodic processes occur simultaneously at the silicon surface [9].

2. Experimental Procedure
The substrate used in my experiment was a 2” p-type, B-doped Si(100) wafer, (0.75-1.25) Ω.cm. The wafer was first cut into pieces with the size of 1 cm² with a diamond cutter. Then the silicon wafer was cleaned with RCA technique to cleanse the surface from grease and debris. To avoid the wafer from being very brittle after etching, scotch tape were stuck onto the bottom surface of the substrate to prevent the bottom surface from being etched during the etching process. A solution consisted of 5 mol/L HF and 0.01 AgNO₃ were prepared in a container. The container used was a plastic beaker and the solution was heated to 60ºC in water bath prepared by filling water in a tray and was placed on top the hotplate. Once the temperature reached 60°C, the silicon wafer was then etched in this solution for 60 minutes and the temperature was maintained during this process. A plastic tweezer was used to hold the wafer during the etching process to avoid the wafer from drifting and floating in the solution. After the etching process the wafer was rinsed with deionized water and was then placed in a glass beaker containing deionized water and cleaned ultrasonically for 60 minutes to detach the thick silver film from wrapping the surface of wafer. Lastly the wafer was rinsed with deionized water again and was then blown dry in air before microstructural observation. The morphology and chemical composition of the sample were characterized with field emission scanning electron microscope (FESEM) and energy dispersive x-ray (EDX).

3. Results and Discussion
Figure (1) shows a cross-sectional SEM image of the etched silicon wafer. It can be seen that the silicon nanowires formed are perpendicular to the surface of the wafer. The etched depth is approximately 20µm and the diameter of the nanowires are in the range of 40-200nm.

Figure (2) shows large area of SiNWs which have a cap-liked structure at the free end. The elemental composition was determined using EDX analysis. Fig. (3) shows the spectrum acquired from etched silicon wafer by EDX analysis. During the etching process, self-assembled localized microscopic electrochemical cell existed in silver nitrate HF solution. The silver deposition happened at the same time as the etching process at the surface of Si wafer took place. In the process of electroless metal
deposition, the silver nanocluster deposited on the surface of silicon wafer to form tree-like dendrites. The deposited silver atoms first form nuclei and then form nanoclusters which were uniformly distributed on the surface of the silicon wafer. The silver nanocluster and the Si area surrounding the silver nuclei acted as a local anodes and cathodes respectively. The electrochemical redox reaction process can be formulated as two half-cell reaction (1) and (2):

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

\[
\text{Si} + 6\text{F}^- \rightarrow \text{SiF}_6^{2-} + 4e-. \quad (2)
\]

The silver nanocluster acted as a cathode was deposited and maintained at the surface of the wafer, while the surrounding silicon acting as the anodes is etched away. Therefore it was said that the nanoscale electrolytic cells leads to selective etching of silicon substrate. As the Ag catalyze the etching reaction, it then sunk below the surface and left behind columns of Si nanostructures with the length of approximately 20µm as shown in Fig. (4).

These nanowires can be used to make chemical sensors by adding two electrodes in between the bundled SiNWs and connecting dc source between the two electrodes. The gas molecules that pass through this sensor device will be adsorbed on the surface of the wires and thus changing the conductance of wires. This chemical sensor is something similar to what Zhou et al. [2] had proposed in their paper where they had produced SiNWs through oxide-assisted growth.

In addition, the etched silicon wafer does have structure similar to nanoporous. As reported in the work of Tucci et al. [10], these nanoporous can be used to fabricate heterostructure devices that show good responses to gas environment due to the interaction of absorbed gas molecules onto depleted porous silicon surface.

However, further studies are needed for utilizing this produced SiNWs as nanoporous to fabricate chemical or gas sensors. This is because the sensitivity of porous silicon depends on porosity, pore structure and size distribution of pores.

4. Conclusion

The selective etching process is an inexpensive and simple way to fabricate SiNWs. This technique is based on electroless metal-particle deposition, where self-assembled localized microscopic electrochemical cell existed in silver nitrate HF solution causing the silicon to be etched away. As a result, SiNW with the length of about 20µm and diameter ranging from 40-200nm were formed. These nanowires have promising characteristic that is useful for the nano electronic and optoelectronic devices.

References