

## **Characterization of Silicon Nanowires Synthesized By Electroless Metal Deposition**

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### **Abstract**

In this work silicon nanowires (SiNWs) are grown on p-type Si wafer surface following a top-down approach. It is a simple electroless metal deposition and wet etching process. The variations in the diameter as well as length of the SiNWs are evident from the scanning electronic microscopic images. Also EDX is carried out and we have found about 97% and 3% for Si and Ag respectively. From X-ray diffraction analysis, it is found that these SiNWs have good crystalline quality with preferred

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growth direction in (400) plane. According to the study of UV spectrophotometer, our synthesized structure shows higher absorption than the bulk Si in the wavelength range of 300 nm to 1100 nm. Similarly the transmittance of SiNWs is found lower than the bulk Si sample. This observation supports that our synthesized structure might be a potential candidate for efficient photovoltaic solar cell and other optoelectronic devices.

## 1. INTRODUCTION

In the last few decades, silicon nanowires (SiNWs) have made an immense impact on various fields and devices like nanoelectronics, nanometrology, biotechnology, bioimaging, biosensors, magnetism, thermoelectric, water splitting and among others. This is partly due to unique properties of SiNWs such as large surface-to-volume ratio (SVR), high aspect ratio, joint density of electronic states near the energies of their Van Hove singularities, enhanced exciton binding energy, high carrier transport mobility, quantum confinement and tunable band structure; which made them more promising than their bulk 3D crystalline counterparts [1-2]. For SVR and quantum confinement properties, nanowires can be used in battery electrodes, chemical sensors, electron emission devices and solar cells. Nanowires can also be used in logic gates, photodetector and Schottky barrier field-effect transistors for its property of thinness (i.e. less than 100 nm) [3]. Moreover, natural abundance of silicon, lack of toxicity, compatibility with mature integrated circuit fabrication techniques, high electron mobility, low reflection and strong broadband absorption give them a priority to use in solar cells [4-5].

Concerning the fabrication of SiNWs, different types of techniques are widely used. To perform the synthesis of SiNWs, various methods can be used such as Electroless metal deposition and etching method (EMDE), Chemical vapour deposition (CVD), Plasma enhanced chemical vapour deposition (PECVD), Laser ablation and Evaporation. However except EMDE, all the above mentioned methods require high temperature along with sophisticated equipment and other austere conditions [6]. In addition EMDE which is also called galvanic displacement method appears to be simple, efficient, and cost effective and there are no requirements for external current, mechanical pressure, vacuum processing or high processing temperature [7-10]. Considering these facilities, in this work EMDE method is chosen for the synthesis of SiNWs.

The synthesized SiNWs are characterized using Scanning Electron Microscope at 5 keV for morphological properties, X-ray Diffractometer for structural properties and UV Spectrophotometer within the range of 300nm-1100nm for optical properties.

## 2. EXPERIMENTAL DETAILS

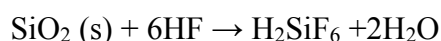
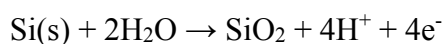
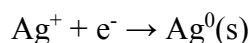
In order to fabricate SiNWs, top-down approach is used. In this approach, at first our Si (100) sample is dipped into a piranha solution [11] (3:1 H<sub>2</sub>SO<sub>4</sub> (97%)/H<sub>2</sub>O<sub>2</sub> (30%))

to obtain a contamination free clean silicon wafer. We can also use ultrasonic bath process instead of piranha solution. However, ultrasonic cleaning process uses high frequency sound waves to create high pressure on the contaminations which adhere to the substrate. This technique can effectively remove contaminations provided that the treatment is carried out for long time, then the crystalline subsurface quality and the wafer performance gradually deteriorates [12]. In our process, at first the silicon wafer is dipped into the acetone solution for 5 minutes and then the wafer is put into an ethanol solution for 5 minutes. Afterwards, the sample is rinsed with deionized water and then dipped into a piranha solution for 10 minutes to remove metals and organic contaminations. In the last step, Si wafer is dipped into HF for 1 minute to remove the native oxide.

Once the cleaning process is completed, samples are dipped into (5M) HF/ (0.02) AgNO<sub>3</sub> solution to get the deposition of Ag nanoparticles. In this way three sets of samples are prepared with 60 sec deposition time and one set of samples is prepared with 120 sec deposition time. Once Ag nanoparticles are deposited on the wafer, then wafers are ready for electroless etching process. In electroless etching process, four sets of samples are immersed in (5M) HF/ (.02M) Fe (NO<sub>3</sub>)<sub>3</sub> solution at the temperature of 26<sup>0</sup> C for the duration of 30 min, 35 min, 50 min and 80 min respectively. Then wafers are copiously rinsed with deionized water and consecutively dried at 88<sup>0</sup> C temperatures to remove the moisture of the sample. All the above steps are done in the Teflon beaker to ensure that the beaker does not add any contamination in the solution as it does not react with HF.

### 3. SYNTHESIS PROCESS OF SILICON NANOWIRE LIKE NANOSTRUCTURE

In EMDE process, at first the Si wafer is immersed entirely in the solution of HF/AgNO<sub>3</sub>. Then the ionized Ag<sup>+</sup> reacts with Si and it becomes neutralized Ag<sup>0</sup>. In this way Ag nanoparticles are deposited on the surface of Si wafer. However there is a formation of SiO<sub>2</sub> underneath Ag nanoparticles, as Si reacts with H<sub>2</sub>O. This formed SiO<sub>2</sub> under Ag nanoparticles are then partially removed by HF present in the solution, leading to pits on the Si surface. These equations are given below-

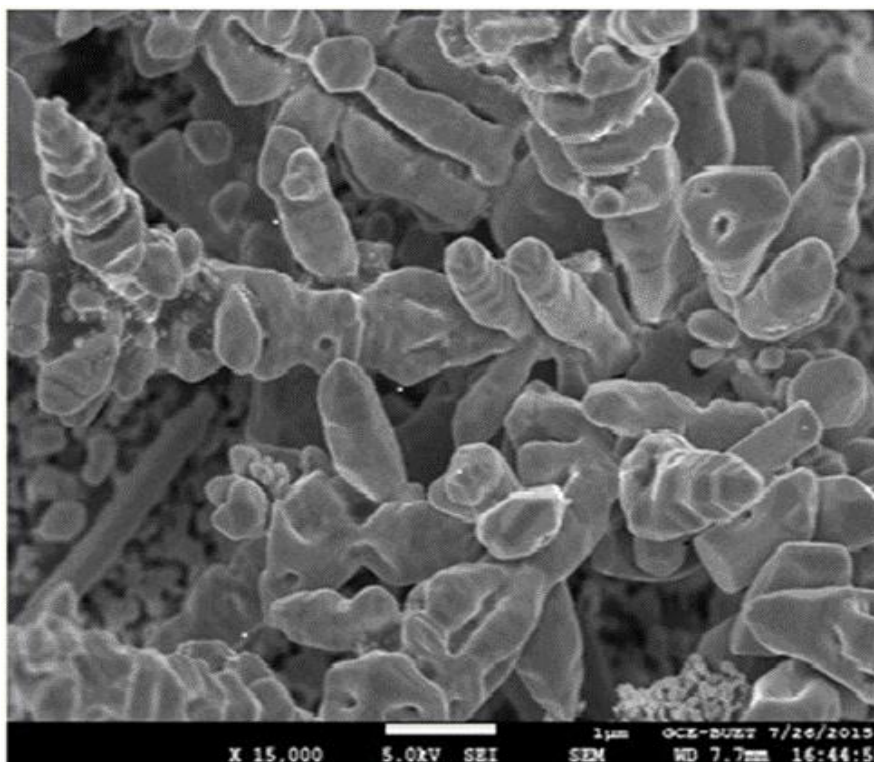


This Si wafer is immersed entirely in the solution of HF/Fe (NO<sub>3</sub>)<sub>3</sub>. In this case the Fe<sup>3+</sup> preferentially obtains electron from Ag nanoparticles and thus it becomes Fe<sup>2+</sup>, whereas the Si underneath the Ag nanoparticles become oxidized to SiO<sub>2</sub>. Thus the continuous removal of SiO<sub>2</sub> eventually etches Si selectively, leads to the formation of

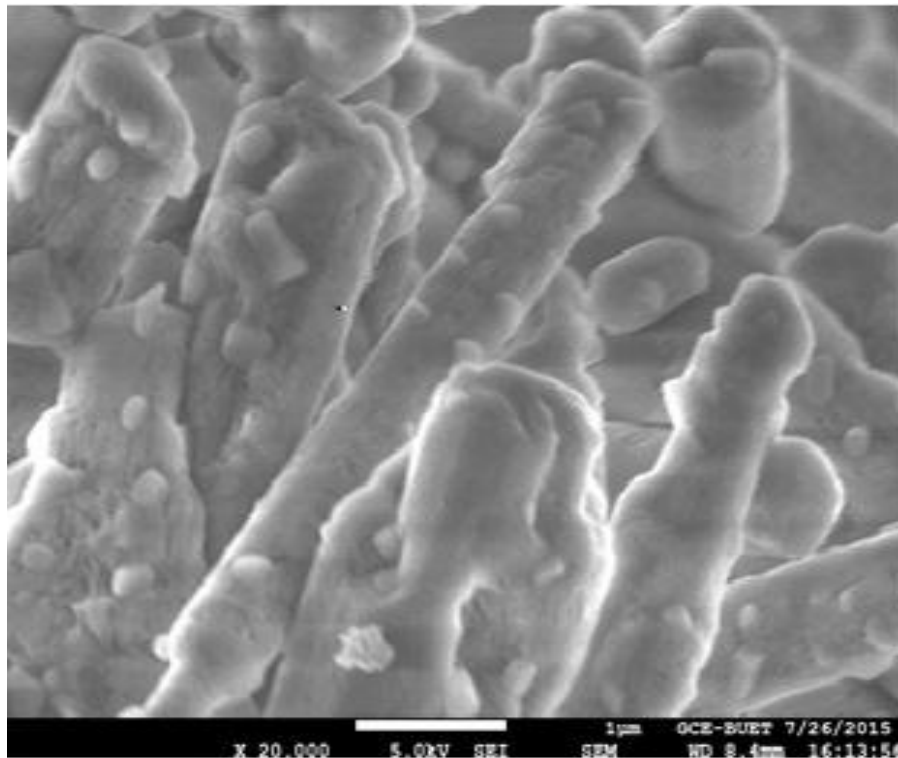
SiNW like nanostructure in the bulk Si. This structure could be considered as Nano rod with reference to dimension of the diameter of the rod. One dimensional nanostructure includes both the wire and rod. It has also been observed that the diameter of nanowires varies from 45nm to 200nm [13].

#### 4. RESULTS AND DISCUSSION

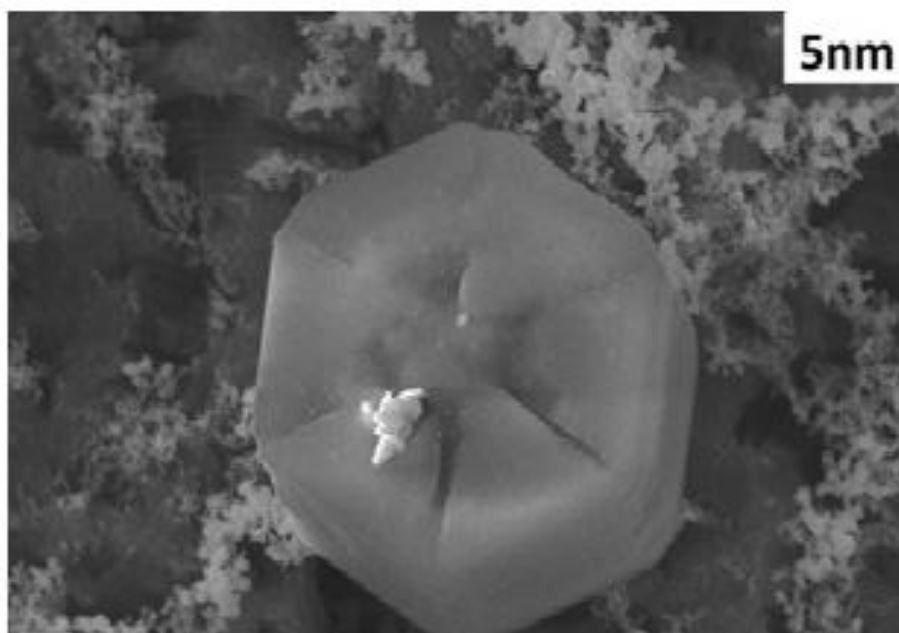
Morphological characterization of SiNW like nanostructures is studied with SEM images of different magnification taken by JEOL JSM- 6490 LA Analytical SEM. The etching morphology of Si wafer likely depends on the morphology of the Ag-particle deposited on it. Moreover, the density and size of SiNWs are greatly influenced by the distributional pattern of deposited Ag particles. In the figure-1 (a, b), the SEM images of the formed SiNWs are showing the branched dendrite structure [6].



1. **Fig. 1(a).** Plane view of dendrite structure of formed SiNWs

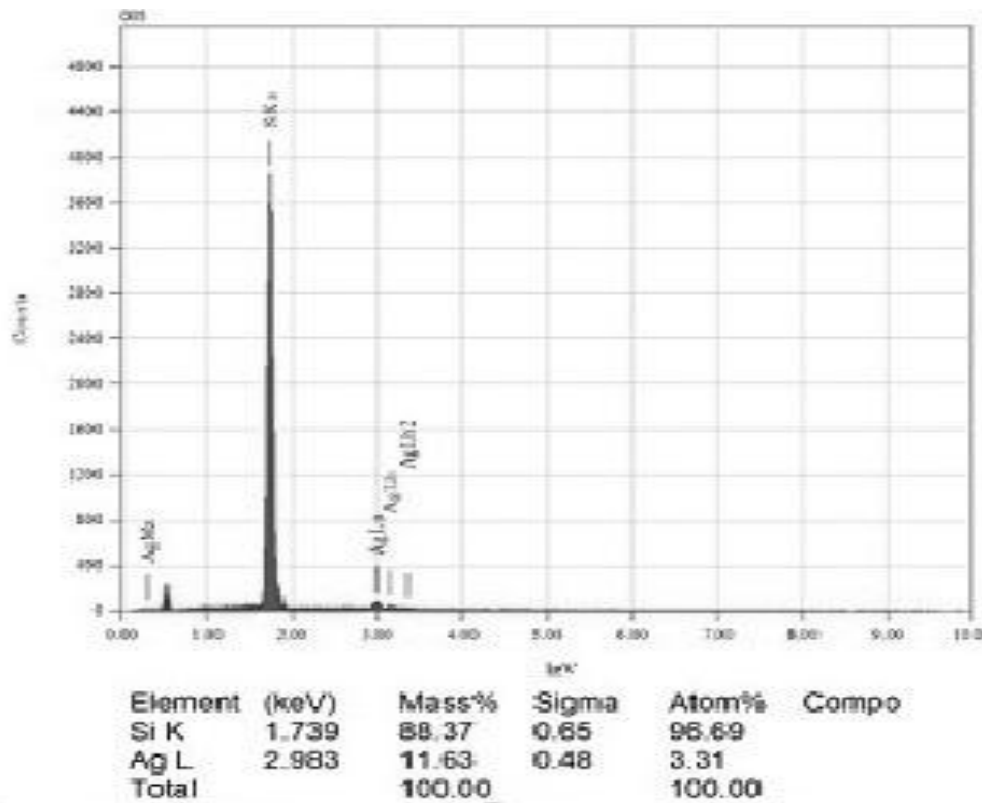


2. **Fig. 1(b).** Tilted view of dendrite structure of formed SiNWs



**Fig. 2.** SEM images of hexagonal SiNWs for the 60 sec Ag deposition duration and 30 min etching duration.

Hexagonal star shaped structure is also evident from SEM image in the present work (figure-2) in which EMDE process is carried out at  $26^0$  C temperatures for 60 sec deposition duration of Ag while the duration for etching is 30 minutes. These hexagonal shaped nanowires are randomly distributed and are preferably vertically aligned on the Si surface. The hexagonal star shaped SiNWs are the thinnest stable Si nanostructures and possess the highest cohesive energy [3, 14]. We observed that excessive deposition time of Ag is destructive for forming SiNWs. Hence the optimized deposition time of Ag is found 60 sec in our work. However, the etching duration is also varied and the optimized etching time is obtained 50 min (Figure1-(a)). EDX is also carried out to see the composition of our samples is shown in figure-3. It reveals the total count for Si and Ag, which are found  $\sim 97\%$  and  $\sim 3\%$ , respectively.

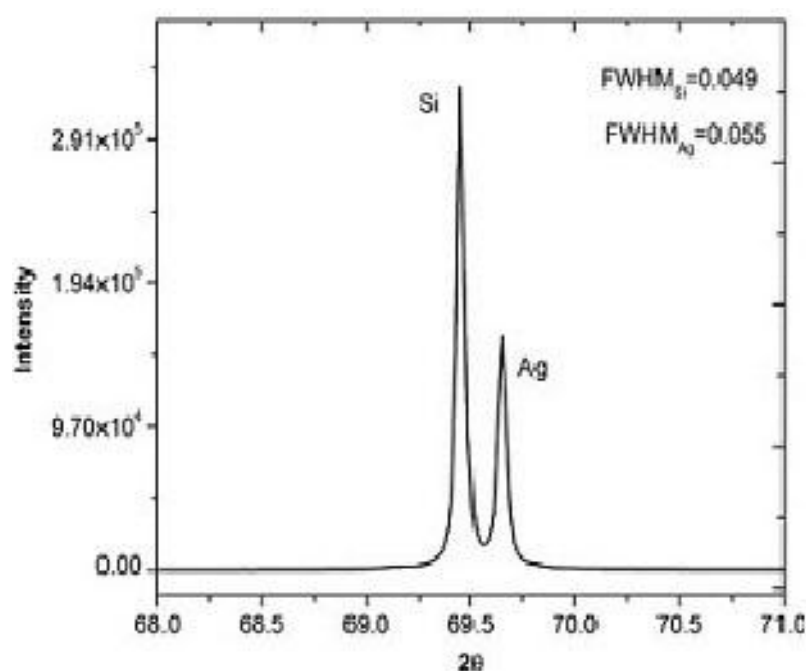


**Fig. 3.** Spectrum acquired from etched silicon wafer by EDX analysis

#### 4.1 Structural properties: X-ray diffraction analysis

After the fabrication of SiNW like nanostructure, x-ray diffraction is performed to know the structural information. For this XRD analysis, a two-circle ( $2\theta$ - $\theta$ ) X-ray power diffractometer (X'pert PRO XRD PW 3040) is used with a  $\text{Cu } k_\alpha$  ( $\lambda = 1573\text{\AA}$ ).

The scanning is performed with a step size of  $0.02^\circ$ , time per step is 1.0 s and scan speed is maintained at a rate of  $1.2^\circ$  per minute. The system is put on operation at 30 mA input current and 40 KV voltages. Figure-4 depicts intensity versus function of  $2\theta$ , for SiNWs fabricated at  $26^\circ\text{C}$  temperature with an etching time of 30 minute. Clearly two peaks at  $69.45^\circ$  and at  $69.65^\circ$  are observed for Si and Ag, respectively. This is in good agreement with the EDX result. Nevertheless, the peak intensity corresponding to Si is higher than the peak of Ag, which is obvious. The well-defined and intense clear peaks with preferred growth direction in (400) plane suggesting the good crystalline quality of SiNWs [15].

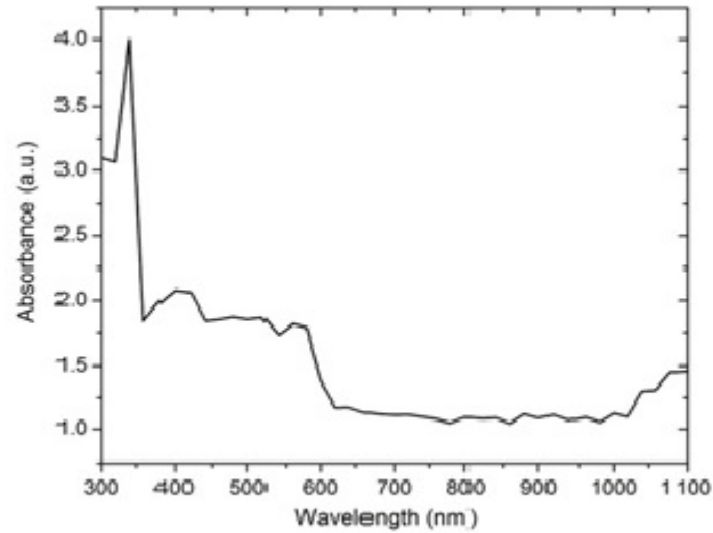


**Fig. 4.** The XRD spectrum of SiNWs.

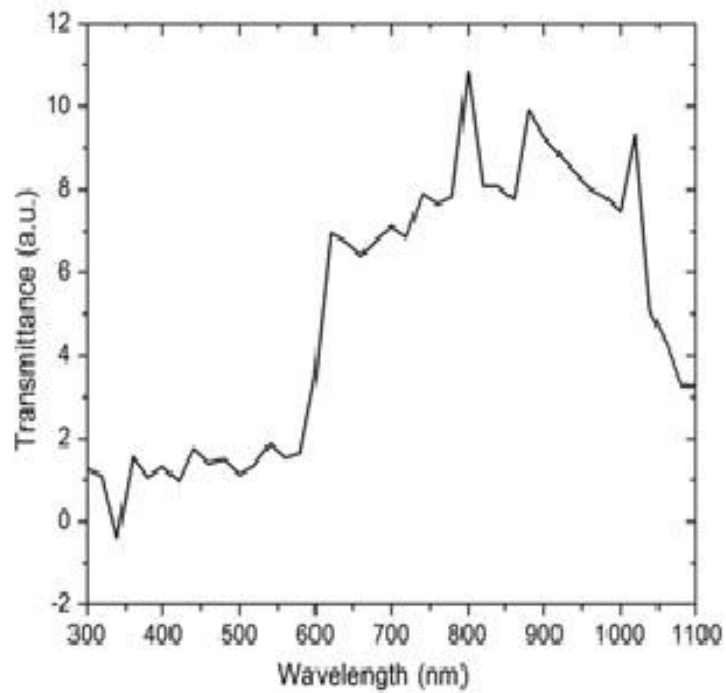
## 4.2 UV Spectroscopy

Fabricated SiNW like nanostructure on the silicon substrate modifies the bulk substrate optical characteristics in the spectral range of 300-2000 nm [16]. The optical characterization of Ag-deposited SiNWs is performed within the spectral range of 300 nm to 1100 nm. As we can see in Figure- 5(a), the SiNWs film has higher value of absorption within the range of 300 nm – 600 nm and then gets lower and almost stable within the range of 600 nm – 1000 nm. It is found that the absorption in SiNWs is more than two orders of magnitude higher than the bulk Si substrate within the same wavelength range. Similarly, in the same wavelength range the transmittance of SiNWs is found more than two orders of magnitude lower than the bulk Si substrate (Figure-5(b)). The light trapping mechanism formed by the array of SiNWs of high aspect ratio lowers the transmittance of the sample by a significant amount. Thus with

higher absorption and lower transmittance, the SiNW films encourage their usage as surface-textured microstructure and anti-reflection coatings [17].



**Fig. 5(a).** The absorption of SiNWs sample in the wavelength range of 300nm to 1100 nm.



**Fig. 5(b).** The transmittance of SiNWs sample in the wavelength range of 300nm to 1100 nm



## 5. CONCLUSION

This experiment demonstrates that electroless metal deposition followed by HF solution based wet chemical etching process is a simple, low cost and effective method to synthesize SiNW like nanostructure with unique optical characteristics. XRD analysis shows that these SiNWs have single crystalline quality. Besides optical absorptions are found to be enhanced compared to bulk Si substrate and significant degradation in transmittance are also observed within the range of 300 nm to 1100 nm. To obtain more uniformity, increased density, desired length, diameter and shape, it is necessary to precisely control over the synthesis process of SiNWs. For strong absorption with lower transmittance properties, SiNWs can be used as antireflection coating in solar cell or for any other important applications.

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