The analysis of fabricated silicon nanowires with various techniques: a roadmap to energy saving world

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Abstract. The fabrication of silicon nanowire has been reported in our research study. The synthesis of functionalized-silicon nanowire (f-SiNWs) array which is currently an intense subject of research with its various vast technological applications. We are presenting here SiNW arrays having various applications in electronic and optical devices which were fabricated by a metal-assisted chemical etching (MACE) of silicon (100) wafers. The varying parameter we have taken for the SiNW growth is its etching duration. Analysis of various deposition parameters has been carried out to optimize the growth of SiNW. Surface morphology of etched Si wafer has been carried out by field effect scanning electron microscopy, Photoluminescence (PL) spectroscopy and XRD. For energy saving world the basic stepping stone is Si based nano regime which is emerging vastly on the basis of silicon nanowire. By analyzing the results we reach in the conclusions that with SiNW we will lead to the energy saving era.

1. Introduction

As we know from today's scenario that large production of electrical growth is being driven by the photo energetic community. So to fulfill this need the manufacturer strived to produce low cost yet well performed high energy photovoltaic panels which can heat large areas [1–3].

As reported by Treuting and Arnold the research in the SiNW field was started around 1957 which till up to now called as first publication on these nanostructures [4]. Later in 1964 Wagner and Ellis gave the approach for the synthesis of SiNW called VLS which is based on the procedure of CVD. After that in the 1990s when the research in this area again came into picture [5–7]. But here comes the major issues like the inefficiency and high cost of conventional solar cells which has emerged as the biggest problem in photovoltaic based electronic technology. So to solve these issues the research group and scientists are heading toward the nanotech community.

Nanostructure material shows great behavior to use as independently and easily combined with thin films. These nanostructures may be (i) 3-D nanocomposites, (ii) 2- D quantum well (iii) 1-D Nanotube (iv) Nanopillar (v) Nanowires, and (vi) 0-D quantum dots. Among these all, nanotubes, nanorods, nanopillars, and nanowires are one dimensional and they show properties such as good absorption of light and high charge separation due to their high surface areas. For getting the high aspect ratio for the exceptional absorption of light the Si and Ge based nanowires fulfill the appealing approach for application in the nano industry [4,8,9].

The implementation and synthesis of SiNWs over the past decade have become a very intense topic to study. The emphasis on one-dimensional silicon nanostructures makes the topic of concentrated research. The reason for attraction toward the SiNW is their excellent electrical and optical properties with a large surface to volume ratio and high aspect ratio which gives a roadmap to the electronic industry such
as photovoltaic cells. With a great abundance of silicon on earth, at the same time silicon-based nanostructures (nanowires) have a high aspect ratio compared to all others as it is reported as 5:1(aspect ratio) [10–12]. As the charge separation approach comes in the picture which leads to less cost, the SiNW material offers valuable importance as PV material. We realize that SiNW can't expand the proficiency yet it can decrease the material that will be utilized for making traditional sunlight based cell consequently the expense of our item get reduced. There is a moment change that comes in this field and an enormous number of techniques have likewise been created. Mainly two approaches are there to synthesize:(i)Bottom-up approach (ii) Top-down approach [13].Bottom-up approach includes VLS(vapor-liquid-solid), thermal evaporation, laser ablation whereas the top-down approach includes patterned lithography technique which collaborates with Reactive ion etching (RIE) and metal assisted chemical etching (MACE) [2,3,14]. From these methods, MACE can be used individually to synthesize SiNW [15,16].

The detailed study about MACE is governed by Li and Bohn in the year 2000. In this method deposition of noble metal on Si substrate has been done, and after that etching took place in a mixture of HF and H2O2, and finally left with porous silicon. At the same time the other groups also improved their synthesis on this groundbreaking work and in the same era costly approaches were also followed. Beside all complex behavior, the MACE is a simpler and exceptional method that fabricate without the utilization of vacuum or high-temperature based equipments Three basic requirements for the following MACE method are (i) HF as a complexing agent (ii) Metal nanoparticles for catalysis purpose (iii) An oxidant which should have high reduction potential than semiconductor material e.g. Silicon. There is quite a similarity between SiNW and carbon nanotubes. Like carbon nanotubes, these are also good field emitters [17], so it is of great attraction to find the field emission properties of SiNW. From the most recent decade, numerous specialists are doing an investigation on the electron field emission properties of SiNW. Li.et.al measured the field emission properties of SiNW prepared with a technique similar to MIE (metal-induced etching). The SiNW which has the diameter of a few nanometers shows the quantum confinement effect (QCE) [18–21]. QCE is dependent upon the size variation of the nanowire similarly, also it has the impact on field emission properties. As future extension the field emission properties of SiNW have been rarely done so ways are still open towards this research field [22].

MACE technique has numerous attributes like minimal effort, simple to control, straightforward which produces silicon nanostructures like nanowires and porous silicon. MACE gave the SiNW having a high aspect ratio, which are uniformly grown, highly crystalline. In our study, the SiNW is investigated using the MACE technique. In the MACE technique, the noble metal used is Ag, Au, Pt, and Pd and here we are using silver (Ag) . There are many methods for deposition ways such as thermal evaporation, sputtering, chemical deposition, etc. Here in our experimentation, we are depositing the nanoparticles by mixing in oxidizing HF arrangement and afterward followed by a chemical etching process.

The two fundamental reasons to utilize sun oriented energy are cost decrease and improving photoelectric effectiveness, which draws scope to examine this field. Since nanowires are on the experimental stage, they have a great role as building blocks for next-generation electronics. The main aim of the present paper is to investigate the size (diameter) by the FESEM technique of the SiNW which are synthesized by the MACE technique, also its photoluminescence spectra and its XRD pattern for the verification of the fabricated sample has been analyzed.

2. Experimental details
Here with the approach of the MACE method the Silicon wafer has been taken which has a resistivity that lies in the range of 5-10 ohm cm. MACE method mainly involves two-step (i) Deposition Process (ii) Etching Process. The deposition mixture is made by the Silver nitrate combined with HF(4.8M) and deionized water. The concentration of HF is 40 % and the AgNO3 we have taken is 0.5mM. The second
part is an etching solution, that is a mixture of HF, hydrogen peroxide, and deionized water. Here the solution we have taken is a combination of 4.6 M HF & 0.5 M H$_2$O$_2$. The hydrogen peroxide we have taken is 30%. At last, the sample is treated with nitric acid to remove the extra silver ion present on the silicon substrate after that we left with SiNWs.

The silicon wafer is firstly cut in the square size of dimension 2cm*2cm. These are ultrasonically treated by dipping in different solutions step by step that is ethanol, deionized water, and acetone for the timing of 20 min each. Then the sample will be dipped with the help of teflon tweezer for the duration of one minute in the deposition solution which contains noble metal Ag, then Ag will be deposited on the Si substrate. To keep the deposition time precise we have used the stopwatch. After dipping again the cleaning of the samples has been done with deionized water. The resulting sample was dipped in an etching solution which contains hydrogen fluoride (HF) and hydrogen peroxide (H$_2$O$_2$) for the duration of 40min. To remove extra silver ion the sample was treated with nitric acid. So we left with the SiNWs nanostructures i.e SiNW on the silicon substrate.

3. Result and discussion

The indication of the formation of the nanowire is given by the rough black color of the Si/AgNPs substrate. In the etching solution, HF/H$_2$O$_2$ the dried samples were dipped. At a different etching time, we dipped the samples in the etching solution. The samples were put in the bottom of the beaker till up to the time as etching time not completed. After each step, the sample should be rinsed in deionized water, and then left to dry. The extra AgNPs were removed when the samples were dipped in nitric acid.

![Figure 1: FESEM images of the top view of Si NWs fabricated by MACE technique](image)
The room temperature PL spectra has been shown in the figure given below that clearly shows peaks at 430 nm, 525 nm and 660 nm. The peak at 410 nm is due to the Si-Si pair and 660 nm originates from electron hole pairs trapped at Si-O bonds. Because band gap is relatively small and indirect, Si usually only emits extremely weak infrared PL at low temperatures. But PL is not observed at room temperature for c-Si. Visible PL of etched wafer followed by an etched duration of 40 min reveals that the band gap of etched Si samples is in the range of 1.9-2.8 eV.

Figure 1(a): SiNW diameter distribution for P type sample having resistivity 5-10 Ohm cm and 1(b) shows data point taken to calculate diameter distribution.

Figure 2: Room temperature PL spectra of P type sample having resistivity in the range of 5-10 Ohm Cm.

Figure 3: XRD spectra of P type sample having resistivity in the range of 5-10 Ohm Cm.
The XRD patterns of the silicon nanostructures fabricated by following etching process has been shown in fig 3. XRD spectra were recorded by using Cu (Kα) radiation (0.15406 nm). The Intensity of main focus was in the range of 2θ =20°–80°. The XRD peak for p type silicon (100) was observed corresponding to lattice planes (400) at 2θ =68.2°, the sharp and narrow diffraction peaks indicate that the silicon nanostructure(Si NS) has good crystallinity. The XRD intensity peak identification was confirmed using JCPDS data, spectra confirmed the crystalline nature of nanoparticles. The other peak was observed indicating defect formation in the etched Si sample as a function of etching time, all reflection plane corresponds to Si -NS with FCC structure. According to Bragg's equation 2dsin θ =nλ where λ is wavelength (Cu Kα radiation (1.5406 Angstrom), n=1, 2, 3. The lattice parameter for Si -NS structure has been estimated by following relation

\[ \frac{d_{hkl}}{a} = \sqrt{h^2 + k^2 + l^2} \]

Since 2dsin θ =nλ so \(d = \frac{nλ}{2 sin θ}\), from equation (1) we get

\[ a = \frac{λ}{2sin θ} \sqrt{h^2 + k^2 + l^2} \]

Lattice parameter, spacing were estimated for intense peak for different concentration using above equation, lattice constant for and p type Si(100) was 0.137 nm, lattice constant increases from bulk lattice constant probably indicated that increase in lattice constant mean the electrons are less bound to the atom, and hence require minimum energy to remove which leads to decreased band gap. Lattice strain in p type Si(100) were estimated using

\[ \text{Lattice strain} = \frac{a-a_0}{a} = \frac{\Delta a}{a} \]

Where a denoted the lattice constant of p type Si(100) while \(a_0\) denoted the bulk lattice constant \(a_0=0.5410\) nm. For Bulk Silicon Lattice strain for p type Si(100) listed in table 1

| Samples | d(nm) | a(nm) | Lattice strain |
|---------|-------|-------|---------------|
| P type Si(100) | 0.138 | 0.685 | 0.21           |

**Table 1.** Lattice parameter of different phase from XRD data

**Conclusion**

The size (diameter) of the SiNW synthesized by MACE technique with etching duration of 40 min on the P type Si substrate having a resistivity of 5-10 ohm cm is 73 nm by the use of Image J software as given in figure 1.a and 1.b. We have investigated the mechanism formation of SiNW during the MACE technique. As the variation in the band gap ranges from 1.9eV to 2.8 eV which opens the door for the photovoltaic industry, as the absorption increases leads to the greater outcome of the light energy. Also the lattice strain is less than that of the bulk counterpart which is also of great use in solar technology industry. Recently there is great use of Si in the solar cell based technology which clearly leads to the energy saving world. The use in the electronic industry comes from these one-dimensional nanostructures, which is a change of light energy to electrical energy. The optical and electrical properties of SiNW make them highly influential nanomaterial. Moreover we can say that SiNWs will be the building block with a great impact for the next generation electronics.
Acknowledgment
One of the authors (Vikas Kashyap) acknowledges financial support (as senior research fellowship) from University Grant Commission (UGC) India.

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