Investigation of Silicon Nanowires Produced by Metal-Assisted Chemical Etching Method

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Abstract. Silicon nanowires (SiNWs) have a strong potential in many fields. The investigation of fabrication methods for SiNWs has attracted much attention in semiconductor applications. This paper proposes a metal-assisted chemical etching (MACE) method as a low-cost and simple method for fabrication of SiNWs. This method is based on the electroless metal deposition (EMD) principle. We have studied the conditions of MACE method for fabrication of SiNWs on (100) p-type silicon wafer. A 0.005 AgNO₃ and 4.8 M HF solution is used for metal-assisted depositing of the silver nanodots. The etching process is achieved by etchant solution consisting of 4.8 M HF and different concentrations of H₂O₂. The effect of etching parameters, such as etching time, H₂O₂ concentration and the dipping time, are investigated. Taguchi with L9 orthogonal array is used by software package MINITAB 17 for designing the experiments. The results of scanning electron microscopy (SEM) observations shows the formation of the silicon nanowires. The effect of the different conditions on the size of the SiNWs is analyzed using S/N ratio and ANOVA approach. The results show that etching time was the most significant factor in the SiNWs fabrication.

Keywords: Metal-assisted chemical etching method, Silicon nanowires, Silver nanodots, Electroless metal deposition, ANOVA, Taguchi method.

1. Introduction

Silicon nanowires (SiNWs) are increasingly attractive for solar cell applications and electronic devices. There are many reasons for using the nanowires in applications such as high surface area-to-volume ratio, activity of the surface and comparable diameter with the Debye screening length (which makes the electrostatically of the surface has the most important effect in carrier conduction). SiNWs has a whisker-like shape with a nanometer scale diameter and length of several micrometers. The electrical characteristics of SiNWs depend on their diameter, length, activity of the surface and doping type[1]. SiNWs can be achieved by two approaches; bottom-up and top-down. In the bottom-up approach, nucleation nanodots are needed to form the preferred nanowires. Chemical vapor deposition (CVD) plasma-enhanced chemical vapor deposition (PECVD), filament-enhanced chemical vapor deposition
(FECVD) and atomic layer deposition (ALD), are among the most important methods in this approach [2][3].

The top-down technique starts with the substrate material(s) upon which the nanowires are formed. There are many means for top-down approach such as photo-lithographical [4] metal assisted chemical etching (MACE) [5][6], electron-beam lithography [7], and reactive-ion etching (RIE) [8].

The bottom-up approach may be ascribed to the vapor-liquid-solid (VLS) growth mechanism [9]. In 2007, the production of Si nanowire by VLS mechanism was achieved for the first time by Kolasinski, using a chemical vapor deposition method. Solid, liquid and gas states are participated in SiNWs growth by VLS mechanism. A liquid state promotes the growth of SiNWs because adsorption of vapor to solid is very sluggish. Gold or aluminum nanoparticles are used as a SiNWs nucleation sites and silane SiH₄ gas is used as vapor reactant. Al-Si or Au-Si alloy liquid is produced by heating the nanodots in the presence of silane at the eutectic temperature. Eutectic alloy spots can be saturated and then super-saturated in silicon by continuous feeding of SiH₄. Thus, in the sufficient super-saturation of silicon, crystal seed starts to grow at the eutectic point-substrate interface.

Figure 1 shows the SiNWs growth mechanism by VLS approach. The diameters of the nanowires are influenced by the size of the nanoparticles, the flow rate and flow duration of silane [10].

![Figure 1](image)

**Figure 1** Vapor-liquid-solid approach for SiNWs fabrication  
(a) nanodots deposition,  
b) SiH₄ decomposition and the eutectic formation,  
c) SiNWs growth through the eutectic point.

Metal-assisted chemical etching (MACE) is a simple and inexpensive method that can be employed for the production of SiNWs in a top-down approach. Nanowires fabricated by this method will have the same crystallinity and doping levels as the bulk. MACE was produced for first time using Al as an promoter metal for SiNWs production [11]. Precursor nanodots on Si substrate acts as catalysts for the etching of silicon in the etchant solution. MACE etching is a redox process in which the cathodic and anodic reactions occur concurrently[12].

Taguchi’s is an important method for designing and analyzing the experiments. It offers a simple, efficient and orderly approach to optimize the experimental parameters [13]. In this work, Taguchi method ANOVA approach is used to determine and analyze the optimal etching parameters with regard to the length of the silicon nanowires.

2. Experimental Method

The substrate used is a P-type single crystal silicon wafer with crystallinity 100. The wafer was cut into 2×2 cm² samples. All samples were cleaned with piranha solution, H₂SO₄ / H₂O₂ 3:1 v/v, then rinsed in DI water. Then they were dipped in HF and DI water, 1:10 v/v, for 2 minutes. 4.8 molarity hydrofluoric acid and 0.005 molarity of silver nitrate solution was used as a source for obtaining the silver nanoparticle. Wafers were placed in silver nanodot source solution for different times (15, 30 and 60 seconds). After the deposition of silver nanodots, the etching process was achieved by solution consisting of 4.8 M hydrofluoric acid and different concentrations of hydrogen peroxide (0.1 M, 0.2 M, 0.3M). The samples were submerged in etchant solution for 2, 5 and 10 minutes.
When the silicon nanowires had been obtained, Nitric and DI water (v:v 1:1) solution was used as silver etchant solution to remove all the silver from the surfaces. Finally, a combination of HF and DI water (v:v 1:10) solution was used for hydrating and cleaning the fabricated SiNWs. In this work, nine experiments were adopted at different factors using Taguchi L9 orthogonal array by the software package MINITAB 17. The SiNWs microstructure was investigated by scanning electron microscopy (SEM). Taguchi analysis and the analysis of variance (ANOVA) have been utilized to study the parameter ranks and to evaluate the influence of these parameters on the sizes of SiNWs.

3. Results and Discussion
MACE mechanism could be summarized in two steps; deposition of nanoparticles (metal-assisted), and etching by galvanic corrosion. Different metals have been used to assist the etching process in this method, of which silver showed the best etching process [14]. HF works as an etchant with H2O2 acting as the oxidant for the galvanic corrosion. The MACE etching mechanism could be illustrated based on catholic and anodic reaction for Ag and Si as it is schematically presented in Figure 2 and displayed by the following reactions [14]:

Cathodic reaction:

$$\text{Ag}^+ + e^- \rightarrow \text{Ag} \tag{1}$$

Anodic reactions:

$$\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4e^- \tag{2}$$

$$\text{SiO}_2 + 2\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O} \tag{3}$$

![Figure 2](image-url)  
**Figure 2**  Metal-assisted chemical etching approach of SiNWs (a) deposition of silver nanodots (b) creation of SiO2 by the catalyst role of silver (c) etching of SiO2 by HF solution and continuous
formation of SiNWs by galvanic corrosion (d) etching of silver nanodots by HNO₃ solution, and (e) Final SiNWs obtained.

Scanning electron microscopy (SEM) can be used to picture materials in nano-scale. Here, SEM is used to investigate the silicon nanowires fabricated by MACE technique. SiNWs nanowire on p-type single crystal silicon substrate was successfully prepared and different lengths of nanowire are attainable by changing the experimental parameters. Figure 3 shows the formation of silver nanodots on the surface of the substrate which will be the nucleation point for having the silicon nanowires as discussed above. Figure 4(a) shows the top view of silicon nanonwires that resulted from the galvanic corrosion process of the surface by the presence of silver nanodots. The separated SiNWs are not clear from the top view images. In order to get a clear view of SiNWs, the holder of the samples for the SEM machine tilted 15° as shown in Figure 4 (b). To measure the SiNWs length, the samples were cut carefully into two pieces to have the edges which show the arrays of SiNWs clearly. Figure 4(c) illustrates.

**Figure 3.** Scanning electron microscopy images of silver nanodots obtained with different magnifications by dipping the specimens in 4.8 M hydrofluoric acid / 0.005 M silver nitrate for 10 seconds as a first step for SiNWs fabrication.

**Figure 4.** Scanning electron microscopy images of SiNWs with different magnifications and different locations for experiment S5: a) The top view (the tilting angle 0°), b) the sample holder tilted 15°, c) The SiNW arrays at the edge of the diced sample.

Table 1 shows the L9 orthogonal obtained by Taguchi method and the SiNWs length for each experiment. Linear regression analysis can be applied, to develop a mathematical model for SiNWs length as shown in Equation 4. The Taguchi method investigates the importance of studying the response variation through the signal-to-noise (S/N) ratio, resulting in minimization of quality characteristic variation due to uncontrollable factors. The SiNWs length was considered as the quality characteristic, with the model of “the-larger-the-better” as shown in Equation 5 [15].
SiNWs’ Length = -0.475 - 0.0550 Dipping Time + 9.17 Etching Conc. + 0.6349 Etching Time \hspace{1cm} (4)

\[
\frac{S}{N} = -10 \log_{10} \left( \frac{1}{n} \sum \frac{1}{x_i^2} \right) \hspace{1cm} (5)
\]

**Table 1** Taguchi Design Experiments and the Results of SiNWs length

| Sample No. | Dipping Time | Etching Conc. | Etching Time | SiNWs Length μm |
|-----------|-------------|---------------|-------------|-----------------|
| S1        | 5           | 0.1           | 2           | 4.90            |
| S2        | 5           | 0.2           | 5           | 7.80            |
| S3        | 5           | 0.3           | 10          | 4.00            |
| S4        | 10          | 0.1           | 5           | 7.40            |
| S5        | 10          | 0.2           | 10          | 2.90            |
| S6        | 10          | 0.3           | 2           | 5.50            |
| S7        | 15          | 0.1           | 10          | 1.25            |
| S8        | 15          | 0.3           | 2           | 5.10            |
| S9        | 15          | 0.3           | 5           | 4.90            |

Figure 5 and Figure 6 show the main effects plots for means and S/N ratios, respectively. It may be observed from Table 4 and Table 5, that show the responses for the means and for the signal-to-noise ratio respectively, the most effective parameter on the process of SiNWs fabrication is the etching time. This is attributed to the effective differences between the values (Delta) for the etching time parameter in comparison with the other two parameters.

**Table 2** Response for means

| Level | Dipping Time | Etching Conc. | Etching Time |
|-------|--------------|---------------|--------------|
| 1     | 4.500        | 3.433         | 1.650        |
| 2     | 4.767        | 4.517         | 4.517        |
| 3     | 3.950        | 5.267         | 6.900        |
Finding which parameter significantly affects the quality characteristic (SiNW size) is the primary goal of ANOVA. This can be done by calculating the total sum of squares SST, the sum of squares within SSW and the sum of squares between SSB as shown in Equations 6, 7, and 8, respectively for each parameter [15]. The significance value α (0.05) is adopted for this study. The degrees of freedom for all the types of the sum of squares (SST, SSW and SSB) are calculated. The degree of freedom within (df_w) will be (n-k) where n is the total number variables and k is the number of variables for each group, so it will be 6. The degree of freedom between (df_b) will be (k-1), so it will be 2. In the same way, the total degree of freedom will be 8. The df_w and the df_b used to determine the critical F-statistics (F_cr) from F-statistics distribution sheet, the F_cr value noticed was 5.14. The mean of the SS_w, MS_w and the mean of the SS_b, MS_b were calculated by dividing each sum of squares by its degree of freedom. The F-statics for each parameter were then calculated by dividing MS_b by MS_w.

Figures, 7, 8, and 9 show the interval plot of SiNWs length vs each parameter. Tables 4, 5 and 6 show the ANOVA (with 95% confidence level) and F-test values with the P (Probability)-value which reflects effectiveness of the individual studied parameters on the SiNWs length. The results indicate that we could not reject the null hypothesis for etching concentration and dipping time parameters, because the values of the F-statics are lower than the F_cr and the P-values higher than the significance factor 0.05. The null hypothesis could be rejected in the case of etching time because the value of the F-statics is higher than the F_cr, and the P-value lower than the significance factor 0.05. The above outcomes have demonstrated that the etching time is the most significant parameter on the SiNWs fabrication by the metal assisted chemical etching time MACE.

\[
SST = \sum (x - \bar{x})^2
\]

\[
SSW = \sum (x - \bar{x})^2
\]

\[
SSB = \sum (\bar{x} - \bar{x})^2
\]
Table 4 Analysis of variance (ANOVA) for the dipping time factor.

| Source | Degree of Freedom | Sum of Squares | Sum of Squares Mean | F-Value | P- Value |
|--------|------------------|----------------|---------------------|---------|----------|
| Between | 2                | 1.041          | 0.5203              | 0.07    | 0.936    |
| Within  | 6                | 46.762         | 7.7936              |         |          |
| Total   | 8                | 47.802         |                     |         |          |

Table 5 Analysis of variance (ANOVA) for the etching concentration factor.

| Source | Degree of Freedom | Sum of Squares | Sum of Squares Mean | F-Value | P- Value |
|--------|------------------|----------------|---------------------|---------|----------|
| Between | 2                | 5.097          | 2.549               | 0.36    | 0.713    |
| Within  | 6                | 42.705         | 7.118               |         |          |
| Total   | 8                | 47.802         |                     |         |          |
Table 6 Analysis of variance (ANOVA) for the etching time factor.

| Source  | Degree of Freedom | Sum of Squares | Sum of Squares Mean | F-Value | P-Value |
|---------|------------------|----------------|---------------------|---------|---------|
| Between | 2                | 41.651         | 20.825              | 20.31   | 0.002   |
| Within  | 6                | 6.152          | 1.025               |         |         |
| Total   | 8                | 47.802         |                     |         |         |

4. Conclusions

The main conclusions of this study are the following:

1- SEM images showed that the chemical etching method was successfully used for producing silicon nanowires (SiNWs) by using silver nanodots as a metal assistant.

2- Taguchi analysis showed the SiNWs’ length increases with increasing of etching time and to a lesser degree with etching concentration.

3- ANOVA results showed the null hypothesis could be rejected in the case of the etching time because the value of the F-statics (20.31) is higher than the Fcr value (5.14) and the P-value (0.002) is lower than the significance factor (0.05).

4- The etching time is the most significant parameter on the SiNWs fabrication by the metal-assisted chemical etching time, MACE.

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References

[1] N. P. R and Alam Muhammad, Design Considerations of Silicon Nanowire Biosensors, *IEEE Trans. Electron Devices*, vol. 54, no. 12, pp. 3400–3408, 2007.

[2] S. Misra, L. Yu, W. Chen, M. Foldyna, and P. Roca I Cabarrocas, A review on plasma-assisted VLS synthesis of silicon nanowires and radial junction solar cells, *J. Phys. D. Appl. Phys.*, vol. 47, no. 39, 2014.

[3] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity, *Chem. Mater.*, vol. 31, no. 1, pp. 2–12, 2019.

[4] M. N. M. Nor, U. Hashim, N. H. A. Halim, and N. H. N. Hamat, Top-down approach: Fabrication of silicon nanowires using scanning electron microscope-based electron beam lithography method and inductively coupled plasma-reactive ion etching, *AIP Conf. Proc.*, vol. 1217, no. 2010, pp. 272–278, 2010.

[5] T. Il Lee et al., A simple and rapid formation of wet chemical etched silicon nanowire films at the air-water interface, *J. Mater. Chem.*, vol. 21, no. 37, pp. 14203–14208, 2011.

[6] X. Li, Metal assisted chemical etching for high aspect ratio nanostructures: A review of characteristics and applications in photovoltaics, *Curr. Opin. Solid State Mater. Sci.*, vol. 16, no. 2, pp. 71–81, 2012.

[7] S. F. A. Rahman, N. A. Yusof, M. N. Hamidon, R. M. Zawawi, and U. Hashim, Top-down fabrication of silicon nanowire sensor using electron beam and optical mixed lithography, *IEEE Int. Conf. Semicond. Electron. Proceedings, ICSE*, no. D, pp. 64–67, 2014.

[8] Y. Q. Fu et al., Deep reactive ion etching as a tool for nanostructure fabrication, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 27, no. 3, p. 1520, 2009.
[9] Y. Wu and P. Yang, Direct Observation of Vapor–Liquid–Solid Nanowire Growth.pdf, no. 22, pp. 3165–3166, 2001.
[10] K. W. Kolasinski, Catalytic growth of nanowires: Vapor-liquid-solid, vapor-solid-solid, solution-liquid-solid and solid-liquid-solid growth, *Curr. Opin. Solid State Mater. Sci.*, vol. 10, no. 3–4, pp. 182–191, 2006.
[11] D. D. S. M. T. N, and K. M, Preparation of thin porous silicon layers by stain etching, *Thin Solid Films*, vol. 297, p. 9, 1997.
[12] A. G. Nassiopoulou, V. Gianneta, and C. Katsogridakis, Si nanowires by a single-step metal-assisted chemical etching process on lithographically defined areas: Formation kinetics, *Nanoscale Res. Lett.*, vol. 6, pp. 1–8, 2011.
[13] W. H. Yang and Y. S. Tarng, Design optimization of cutting parameters for turning operations based on the Taguchi method, *J. Mater. Process. Technol.*, vol. 84, no. 1–3, pp. 122–129, 1998.
[14] K. Peng et al., Fabrication of single-crystalline silicon nanowires by scratching a silicon surface with catalytic metal particles, *Adv. Funct. Mater.*, vol. 16, no. 3, pp. 387–394, 2006.
[15] S. Rama Rao and G. Padmanabhan, Application of Taguchi methods and ANOVA in optimization of process parameters for metal removal rate in electrochemical machining of Al/5% SiC composites, *Int. J. Eng. Res. Appl.*, vol. 2, no. 3, pp. 192–197, 2015.