# Application of taguchi's design of experiments in optimization of metal assisted chemical etching process

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# Application of taguchi's design of experiments in optimization of metal assisted chemical etching process

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**Abstract.** In this study, statistical analysis using Taguchi's method was used to investigate the effects of various process parameters involved in metal assisted chemical etching (MACE) of silicon. The process parameters that include etching time and various etchant concentration were selected and visualized in Taguchi modelling. Each sample was then characterized using the field emission scanning electron microscopy (FESEM). All data was then analysed and evaluated using ANOVA and graph modelling in order to visualize the interaction of each model. Results showed that for etching rate, separation and size of Si nanowires, the predicted model is in agreement with the experimental data with $R^2$ of 0.94, 0.99 and 0.98 respectively.

## 1. Introduction

Design of experiment (DOE) is a planned approach for determining cause and effect relationship. It is a mathematical tool used to investigate the importance of specific process or product variables and how to control them to optimize the system performances while maximizing properties. Moreover, it uses statistical methodology to analyse data and predict process and product performances under all possible condition within the limit selected for experimental design. DOE result also provided a clearer understanding of the product parameter and their interaction in experimental studies. Furthermore, all of this is run under minimal cost of engineering runs, time and money. In this study, the aim of DOE is to optimise the parameters involve in metal assisted chemical etching (MACE) of silicon (Si).

There are various approaches in DOE and one of it is the Taguchi's method. This method was developed by Gen'ichi Taguchi using orthogonal arrays for the experimental setup where only a minimum number of experiments were needed [1]. In this study, Taguchi's method was used to optimize the metal assisted chemical etching of Si. Metal assisted chemical etching is a simple and low-cost method for fabricating various Si nanostructure with the ability to control various parameters such as the etchants concentration, etching time and temperature while offering better controllability of structural parameters [2, 3]. Hence, the Taguchi's method is useful and can be applied in Si etching

to find a proper process method and data experiment required [4]. In this study, model development and simulation were done by using Design expert 7.1 software. In optimization of the metal assisted chemical etching process, it is important to see which parameters are statistically significant where the optimal combination of the process combination can be predicted [5]. The responses were studied in order to identify the optimized value for each parameter. Responses measured were etching rate, length, separation, size and the uniformity of the nanowire structures.

## 2. Materials and method

The Si nanostructures were synthesized on a single-crystalline [100] p-type wafer. Initially, the wafers were dipped in natrium hydroxide (NaOH) solution for damage removal. Following damage removal, wafer cleaning was carried out in RCA-1 and RCA-2 solution to remove metal ion and organic residue from the silicon wafers. Etching was done by immersing the silicon wafers in a mixture of hydrofluoric acid (HF), silver nitrate ($AgNO_3$) and hydrogen peroxide ($H_2O_2$) aqueous solution at various times and concentrations at room temperature. The prepared samples were then immersed in diluted nitric acid ($HNO_3$) solution for about two to five minutes to remove any silver residue. Finally, the samples were cleaned with deionized water and dried using nitrogen gas. The morphological properties of the silicon wafers were observed using field emission scanning electron microscopy. (FESEM). Details etching method was discuss elsewhere in a study by Azhari et al. [6].

In this study, four factors with three levels were evaluated using the Taguchi's Method. Table 1 shows the parameters and levels under study. From the model simulation, the number of experimental runs with the parameter condition were generated. Results from the experiment were analysed by using the analysis of variance (ANOVA) to determine the significance of each parameters and the relationship between the parameters. Finally, model optimization was carried out to obtain optimize value for each design parameters.

**Table 1.** Parameters and levels involve in the study

| Parameters | Level | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $AgNO^3$ (M) | 0.01 | 0.03 | 0.05 |
| HF (M) | 1.0 | 5.0 | 10.0 |
| $H_2O_2$ (M) | 0.15 | 0.25 | 0.50 |
| Time (min) | 30 | 60 | 100 |

## 3. Results and discussion

From the model simulation the number of experiments conducted were reduced to only 9. Each parameter was denoted as A, B, C and D representing the concentration of $AgNO_3$, $H_2O_2$, HF and etching time respectively.

### 3.1. The effect of etching time and etchant concentration

There were five responses measured in this Taguchi modelling; the etching rate, the length, size, separation and the uniformity of the Si nanowires formation. Figure 1 shows the results of etching process at various concentration of $AgNO_3$, $H_2O_2$ and HF for the duration of 100 minute. All etching was conducted at room temperature (27°C). It was observed that at very low HF concentration (1 M) no formation of nanostructures was observed. Study by Kato and Adachi [7] denoted that at very low HF concentration, the formation of Si nanowires was very slow while very high concentration of HF led to the destruction of the Si nanostructures. This phenomenon is explained by the molar ratio (ρ) dependent on the etching behaviour of the Si nanostructures as discuss by Chartier et al. [8]. High proportion of HF concentration (100% > ρ > 70%) leads to the formation of straight pores with diameter identical to the size of the Ag nanoparticles. Decreasing concentration of HF results in the formation of almost cone shape structures with wide opening at the surface while low concentration of HF (ρ < 30%) leads to the formation of cone shape structures covered with micro-pores. This suggests

that the molar ratio between HF and $H_2O_2$ plays an important role in determining the desired Si nanostructures. An optimum proportion of both etchants is needed in order to get well-defined high aspect ratio Si nanostructures.
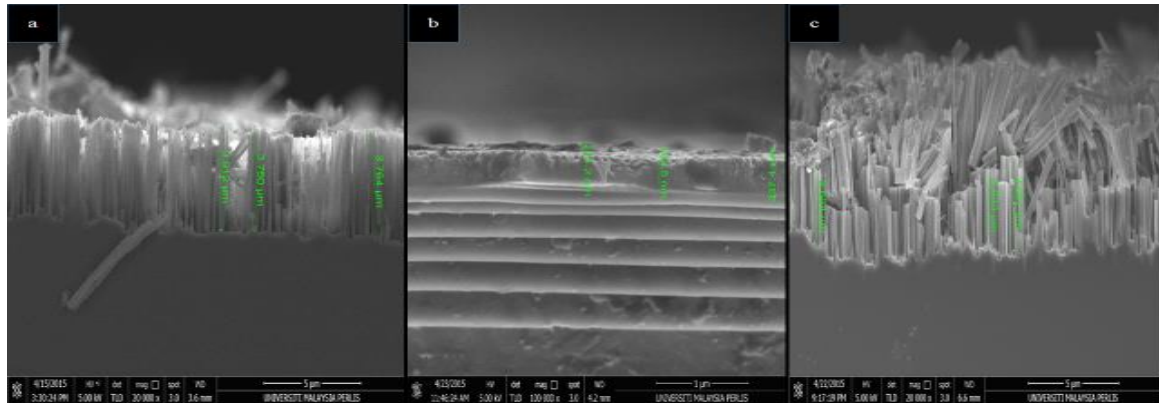


**Figure 1.** Length of nanowire at 100-minute etching time (a) $AgNO_3$ 0.05 M, HF 10 M and $H_2O_2$ 0.5 M, (b) $AgNO_3$ 0.03 M, HF 1 M and 0.25 M, (c) $AgNO_3$ 0.01 M, HF 5.5 M and $H_2O_2$ 0.15 M.

In Figure 2, it was observed that when the concentration of $AgNO_3$ was low (0.01 M) no formation of nanowires were observed, while at higher concentration (0.05 M), destruction of the nanowires was evident. Eventually, high concentration of Ag leads to higher etching rate. However, if the concentration of metal catalyst is too high, the whisker like structures are less prominent and are often replaced by porous microstructures [9]. A related study by Kato et al., demonstrated that when the concentration of Ag was higher than 0.08 mol/L, the height of the nanowires starts to decrease. When the concentration of Ag was more than 0.1 mol/L, no formation of nanostructures is observed, instead formation of rough surfaces was observed [7]. However, even when the concentration of $AgNO_3$ was low, etching of the Si nanowires still exist if the concentration of HF was high as can be seen in Figure 3 (c).
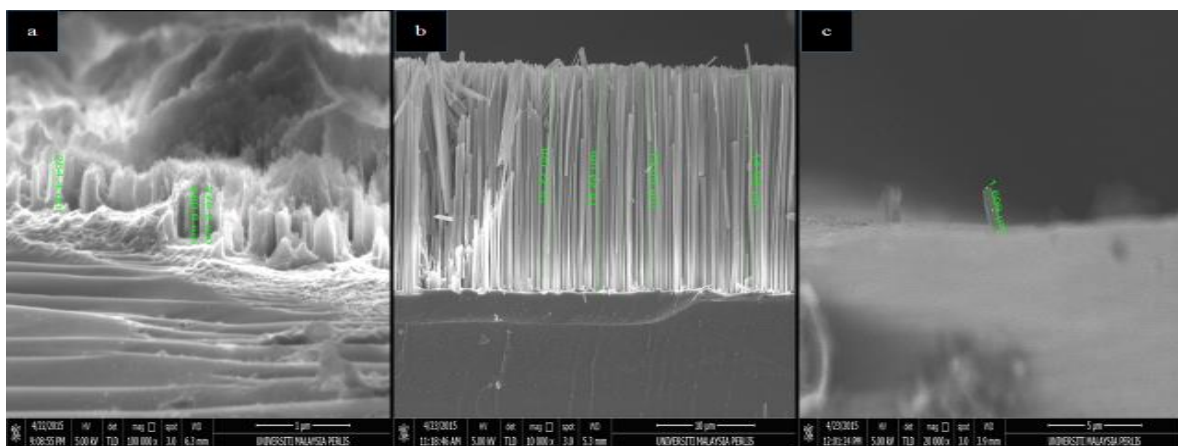


**Figure 2.** Length of nanowire at 60-minute etching time (a) $AgNO_3$ 0.05 M, HF 5.5 M and 0.25 M $H_2O_2$, (b) $AgNO_3$ 0.03 M, HF 10 M and $H_2O_2$ 0.15 M, (c) $AgNO_3$ 0.01 M, HF 1 M and $H_2O_2$ 0.5 M.
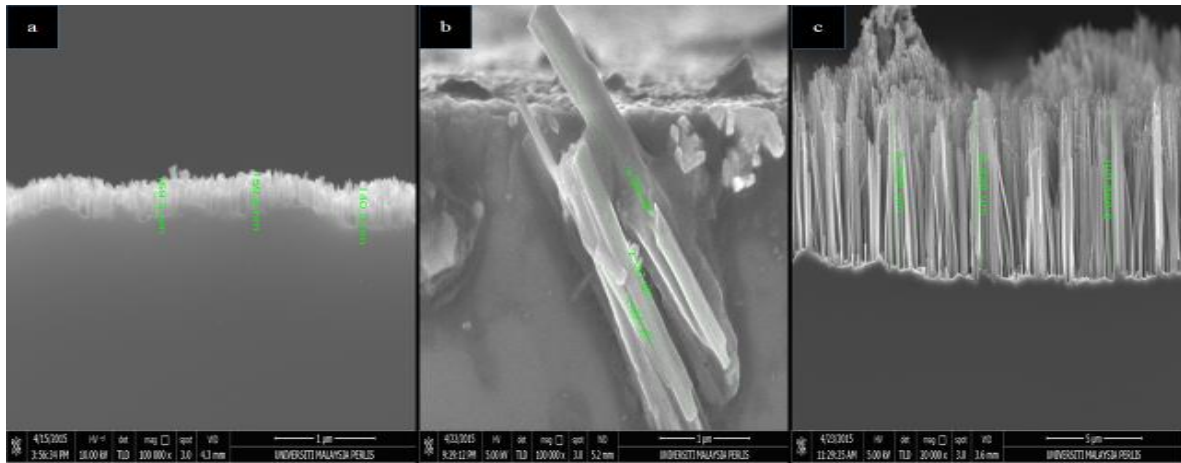
**Figure 3.** Length of nanowire at 30-minute etching time (a) $AgNO_3$ 0.05 M, HF 1 M and $H_2O_2$ 0.15 M, (b) $AgNO_3$ 0.03 M, HF 5.5 M and $H_2O_2$ 0.5 M, (c) $AgNO_3$ 0.01 M, HF 10 M and $H_2O_2$ 0.25 M.

*3.2. Etching rate*

The analysis of variance (ANOVA) on the relationship between the etching rate and the model parameters (Table 2) depicted that the etching rate was highly affected by the concentration of $H_2O_2$ and HF. This was denoted by the low p-value of less than 0.05 for the overall model and individual parameters. The result was in agreement with the predicted data as indicated by the high $R^2$ of 0.939.

This can be explained by first understanding the electrochemical process underlying Si etching. When Si wafer is immersed in the etchant solution, several reduction reaction are involved. When subjected to solution of oxidation process, $H_2O_2$ reacts with Ag particles to form $Ag^+$ ions, which later convert back into Ag particles through oxidation reaction with Si. The oxidation of Ag by $H_2O_2$ also promotes nucleation of smaller Ag nanoparticles that are subsequently deposited on the surfaces and sidewalls of the Si nanostructures [10, 11]. This leads to lowering of etching rate as a function of time due to depletion in concentration of Ag+ ions. In contrast, high concentration of $H_2O_2$ accelerates the production of Ag+ ions thus increasing the etching rate. However, after a certain time, the etching rate starts to decrease due to reduction in Ag particles and $Ag^+$ ions supply. This is in agreement with previous studies by [8, 12].

**Table 2.** ANOVA table for etching rate.

| Source | Sum of Squares | df | Mean Square | F Value | p-value (Prob > F) | |
|---|---|---|---|---|---|---|
| Model | 4.25E+06 | 4 | 1.06E+06 | 15.40 | 0.0107 | Significant |
| B-$H^2O^2$ | 2.54E+06 | 2 | 1.27E+06 | 18.39 | 0.0096 | |
| C-HF | 1.71E+06 | 2 | 8.55E+05 | 12.40 | 0.0193 | |
| Residual | 2.76E+05 | 4 | 68932.43 | | | |
| Cor Total | 4.52E+06 | 8 | | | | |
| | | | | | | |
| Std. Dev. | 262.55 | R-Squared | | 0.9390 | | |
| Mean | 1325.92 | Adj. R-Squared | | 0.8780 | | |
| C.V. % | 19.80 | Pred. R-Squared | | 0.6912 | | |
| PRESS | 1.40E+06 | Adeq. Precision | | 11.8800 | | |

The effect of various model had been graphically plotted in one factor graph in order to determine the interaction of the etching rate with the parameters significant in this model. Figure 4 shows the

one-factor graph for etching versus the HF and $H_2O_2$ concentration respectively. From the graph, it was apparent that the etching rate increases with the increased in HF and $H_2O_2$ concentration.
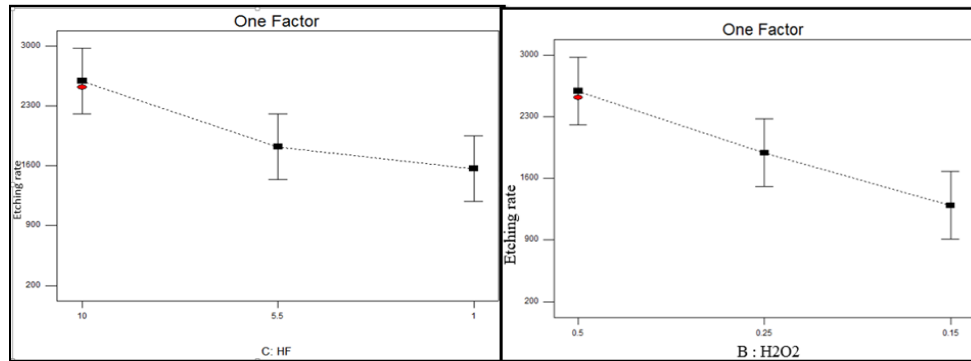


**Figure 4.** One factor graph plot on the effect of $H_2O_2$ and HF on etching rate.

*3.3. Separation*

The effect of various model parameters on the separation of nanowires formation was evaluated using statistical data analysis ANOVA as shown in Table 3. Result from the reduced model analysis suggest that the model is significant with an $R^2$ of 0.9992. The table also showed that the p-value for the overall model and the A, B, and C model parameters was equal to 0.0025, 0.0029, 0.0083 and 0.0014 respectively indicating that A, B and C were the significant model parameters in controlling the separation of the Si nanowires.

**Table 3.** ANOVA table for separation.

| Source | Sum of Squares | df | Mean Square | F Value | p-value (Prob > F) | |
|---|---|---|---|---|---|---|
| Model | 108.2 | 6 | 18.03 | 393.3 | 0.0025 | significant |
| A-AgNO$^3$ | 31.41 | 2 | 15.71 | 342.53 | 0.0029 | |
| B-H$^2$O$^2$ | 10.92 | 2 | 5.46 | 119.06 | 0.0083 | |
| C-HF | 65.87 | 2 | 32.94 | 718.32 | 0.0014 | |
| Residual | 0.092 | 2 | 0.046 | | | |
| Cor Total | 108.29 | 8 | | | | |
| | | | | | | |
| Std. Dev. | 0.21 | R-Squared | | 0.9992 | | |
| Mean | 10.72 | Adj. R-Squared | | 0.9966 | | |
| C.V. % | 2.00 | Pred. R-Squared | | 0.9829 | | |
| PRESS | 1.86 | Adeq. Precision | | 65.459 | | |

From the one factor graph for separation in Figure 5, the models showed that various concentration of $H_2O_2$ were fitted with the design point. The separation of nanowires increases as the concentration of $H_2O_2$ increases. However, it was observed that low HF concentration (less than 5 M) had no effect on the separation of the nanowires but when the concentration of HF was increased, the separation between the nanowires were also increased. On the other hand, the concentration of $AgNO_3$ were inversely proportional with the separation size where low concentration of $AgNO_3$ resulted in increasing of the separation.
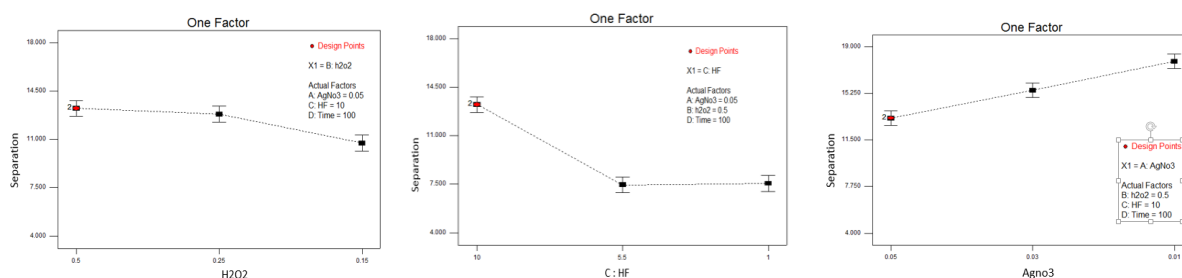
**Figure 5.** One factor graph plot on the effect of $H_2O_2$, HF and $AgNO_3$ on separation.

*3.4. Size*

The various effect of model parameters on determining the size of the Si nanowires were evaluated by ANOVA and was depicted in Table 4. Result from the reduced model showed a significant relationship between the model with an $R^2$ of 0.9842. .

**Table 4.** ANOVA table for size.

| Source | Sum of Squares | df | Mean Square | F Value | p-value (Prob > F) | |
|---|---|---|---|---|---|---|
| Model | 1.98E+05 | 6 | 33065.79 | 20.74 | 0.0467 | Significant |
| B-$H^2O^2$ | 49302.42 | 2 | 24651.21 | 15.46 | 0.0608 | |
| C-HF | 1.43E+05 | 2 | 71458.62 | 44.82 | 0.0218 | |
| Residual | 3188.98 | 2 | 1594.49 | | | |
| Cor Total | 2.02E+05 | 8 | | | | |

| | | | | |
|---|---|---|---|---|
| Std. Dev. | 39.93 | R-Squared | 0.9842 | |
| Mean | 186.31 | Adj. R-Squared | 0.9367 | |
| C.V. % | 21.43 | Pred. R-Squared | 0.6797 | |
| PRESS | 64576.76 | Adeq. Precision | 12.803 | |

The effect of size as a function various model was described graphically in the one factor graph. From the plotted data shown in Figure 6, the size of nanowires is inversely proportional with the concentration (B) $H_2O_2$. While the size of the Si nanowires increases approximately linear with the concentration of HF.
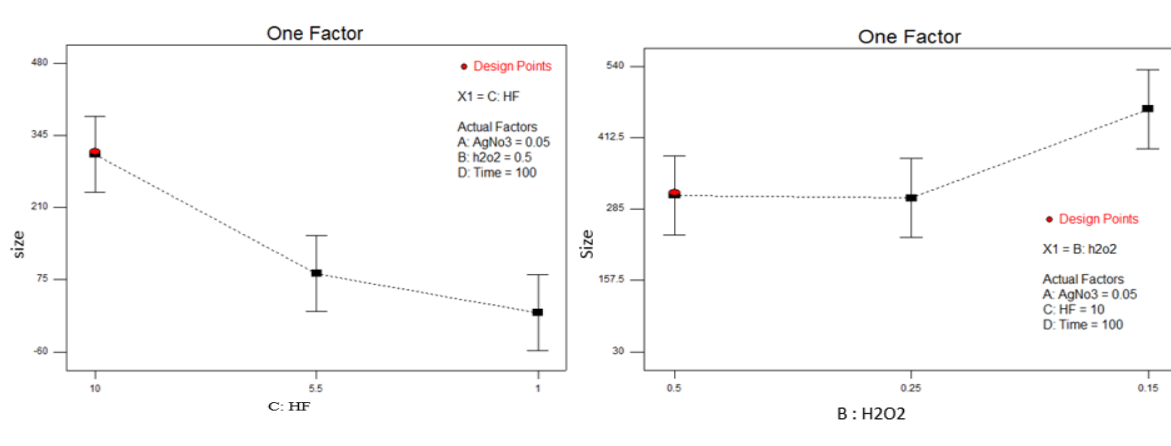


**Figure 6.** One factor graph plot on the effect of $H_2O_2$ and HF on size.

*3.5. Design optimization*

From the design optimization model, 3 set of optimized process parameters were determined. The parameters and optimized levels were as shown in Table 5. Based on the optimization process, the optimum concentration of Ag, HF and $H_2O_2$ was 0.05 M, 10 M and 0.15 M respectively. At this concentration, the etching rate, length and size of silicon nanowires was estimated to be maximize and the separation of nanowires was minimized.

**Table 5.** Optimized design model.

| No. | AgNO$_3$ | H$^2$O$^2$ | HF | Time | Etching Rate | Length | Separation | Size | Desirability |
|-----|----------|------------|-----|------|--------------|--------|------------|------|--------------|
| 1 | 0.05 | 0.15 | 10 | 100 | 1292.29 | 100480 | 115.108 | 464.043 | 0.661 |
| 2 | 0.05 | 0.15 | 10 | 60 | 1292.29 | 75570.1 | 115.108 | 464.043 | 0.612 |
| 3 | 0.05 | 0.15 | 10 | 30 | 1292.29 | 68438.8 | 115.108 | 464.043 | 0.596 |

## 4. Conclusions

From this study, it can be concluded that the etching rate and the nanowires formation is affected by the etchant concentrations and the etching time. A balanced etchant concentration is needed as it will affect the formation of the desired Si nanowires structures. Overall, this study has successfully optimized the parameters for silver etching by using Taguchi application using L9(orthogonal array). The parameters and levels in this Taguchi modelling are significant for the determination of the etching rate, size and separation of the nanowires formation.

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