



## Characterization of Si nanowires synthesized using metal-assisted wet-chemical etching

Eman S. M. Ashour<sup>1\*</sup>, M.Y.Sulaiman<sup>1</sup>, N. Amin<sup>2</sup>, Z. Ibrahim<sup>3</sup>.

<sup>1</sup> Solar Energy Research Institute (SERI),UKM, Malaysia, <sup>2</sup> Faculty of Engineering and Built Environment, UKM, Malaysia , <sup>3</sup> Faculty of Science and Technology, UKM, Malaysia.

Received 1 November 2012, Revised 28 January 2012, Accepted 21 February 2012, Available online 28 April 2012

### ABSTRACT

A synthesis of vertical silicon nanowire array through metal-assisted chemical etching of highly doped p-type silicon wafers (100) in a solution of hydrofluoric acid and silver nitrate has been proposed. . The influences of the growth parameters such as solution concentration, etching time have been investigated. In addition, we consider other common parameters like wafer resistivity and temperature, which rely on the silicon nanowires formation. The results indicate that the silicon nanowires retain the single crystalline structure and crystallographic orientation of the starting silicon wafer. Furthermore, They provide excellent antireflection property with a low reflection loss of 3% for incident light within the wavelength range of 200–900 nm. Such nanowire arrays may have potential applications as antireflection surface for silicon solar cells

| silicon nanowires | silver nitrite catalytic | reflectivity | etching |

© 2012 Ibnu Sina Institute. All rights reserved.  
<http://dx.doi.org/10.11113/mjfas.v8n3.138>

### 1. INTRODUCTION

In recent years, One-dimensional nanostructures have attracted much attention not only because of their interesting structural, electronic and optical properties but also because of their unique applications in mesoscopic physics and fabrication of nanoscale devices ( 1,2). To date, Silicon based one dimensional nanostructure have been broadly explored for a wide range of applications such as field effect transistors (3), photodetectors(4), light emitting diodes (5), biosensors(6), lithium batteries (7), thermoelectric systems (8) and solar cells( 9).

In order to realize these applications, controllable, high quality and cost effective nanowires growths are of significant importance. Much attention has been paid to the growth of Si nanowires; so Many synthetic strategies have been successfully developed to obtain vertical arrays of SiNWs, using both the bottom-up and the top down approaches. The most commonly used bottom-up Si NW production method is the vapour–liquid–solid (VLS) (10) method by chemical vapour deposition (CVD). Other alternatives, such as molecular beam epitaxy , thermal evaporation , supercritical fluid–liquid–solid (11) and laser ablation (12), all have been reported to produce Si NWs.

All of these methods are accessible and well controlled; nevertheless they require high temperature, high vacuum, toxic silicon precursors and complex equipments

which prompt them to be immature choice for silicon nanowire production.

On the other hand, Si NWs can also be fabricated by top-down approaches via reduction of bulk silicon. Top down approach include different methods like lithographic methods (13), direct reactive ion etching (DRIE) (14) and wet-chemical etching ( 15-16).

As a top-down approach, metal-assisted wet-chemical etching of silicon substrates is considered as a promising method to achieve precise positioning of aligned SiNWs as well as control of diameter, length, spacing, and density, avoiding high-cost and low-throughput conventional lithographic processes.

Considering these great features, metal-assisted wet-chemical etching method is expected to become the leading technique to produce Si NWs arrays.

In the present work, the realization and characterization of SiNWs based on metal-assisted wet-chemical etching fabrication method is presented and investigated. We study the process parameters, including the time (up to 2 h), temperature (within 25–100 °C) , etching solution concentration and the nature of the substrate (such as doping type, density and crystallinity).The SiNWs arrays show a low reflectance loss of 3% within the wavelength range of 200–9,00 nm. Based on their excellent antireflection property, they may have potential applications as antireflection surface for silicon solar cell applications.

Corresponding author at:

E-mail addresses: [emansad12@gmail.com](mailto:emansad12@gmail.com) (Eman Ashour)

## 2. EXPERIMENTAL

Growth of aligned SiNW arrays was carried out on p-type (100) silicon (0-1Ωcm) wafers. The etching was carried out in a Teflon beaker containing HF /AgNO<sub>3</sub> solution, varying etching parameters like concentration, temperature as well etching time. Prior to the etching, the samples were sequentially cleaned with acetone, ethanol and de-ionized water for 5 minutes each. Followed by cleaning with boiling piranha solution (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> = 3:1 by volume, for 60 min) to remove any organic containment. The samples were then rinsed thoroughly with de-ionized water followed by dipping in 10% HF solution to remove any surface oxides. The cleaned silicon wafers were then immersed in the etching solution. After the etching processes, the tree like silver pattern wrapping the silicon samples were detached by NH<sub>3</sub>OH /H<sub>2</sub>O<sub>2</sub> (3:1) solution.

Finally, samples were rinsed with deionized water and blown dry in air. It is worth to mention that Morphology of the samples was examined by scanning electron microscope (SEM; LEO 440VP). The structure and chemical composition of the samples were investigated with energy dispersive X-ray spectrometer (EDS) (EDAX company, USA).

## 3. RESULTS & DISCUSSION

Typical cross section view SEM images of the SiNWs arrays prepared by metal-assisted wet-chemical etching is shown in Figure1 (a).

It can be clearly seen that we have vertical aligned SiNWs over the whole silicon surface. SiNWs uniformity over the entire surface are confirmed using AFM views (Fig 1(b)).

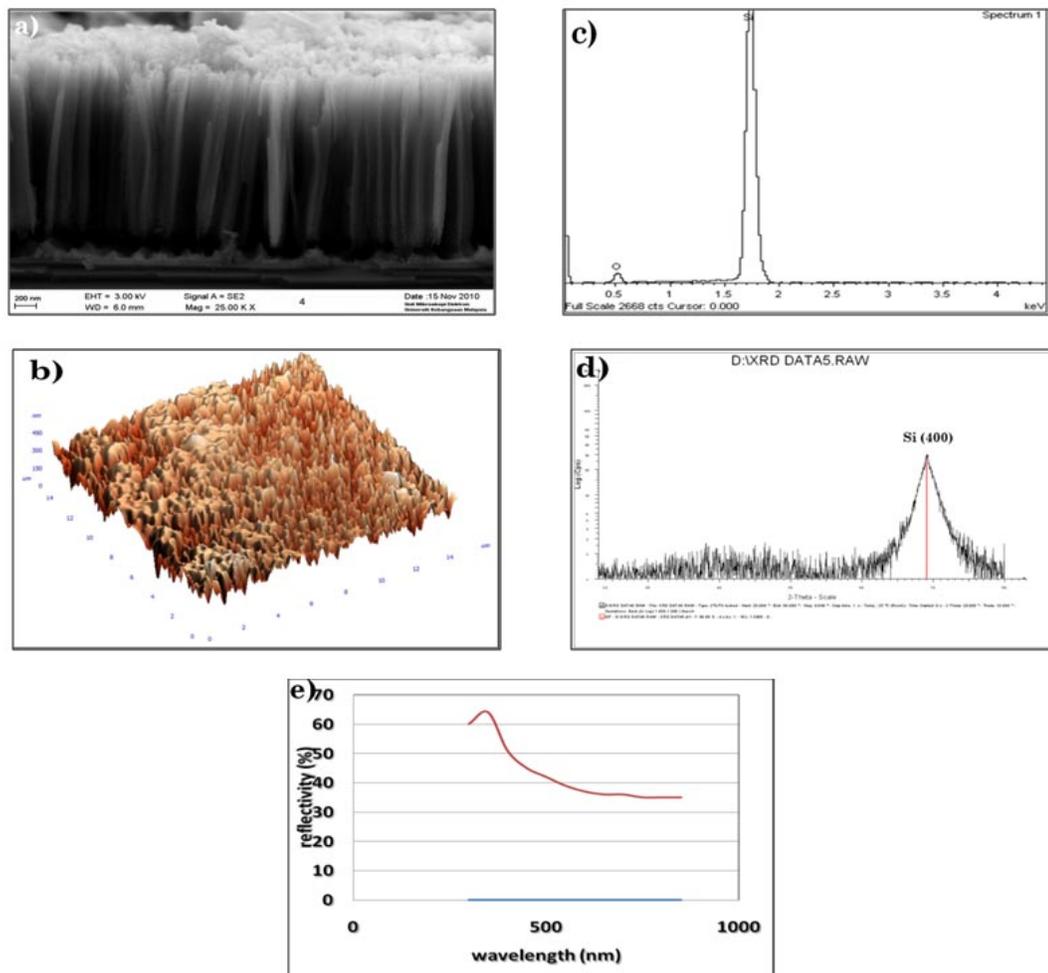


Fig. 1 a). cross-sectional SEM images of SiNWs prepared by metal-assisted wet-chemical etching for 30 min in HF/AgNO<sub>3</sub> ( 5.25M/0.02M) at 50°C. b). AFM image of SiNWs obtained under same condition. c). EDS image of SiNWs obtained under same condition. d). X-ray diffraction image of SiNWs obtained under same condition. e). Reflectivity spectrum of a bare of silicon and SiNWs etched under same condition.

The representative EDS spectrum of the SiNWs after cleaning is shown in Fig 1(c). The strongest signal

observed corresponds to silicon reconfirming that the nanowires are made purely of silicon and no silver

impurities are observed. The signal corresponding to O is attributed to oxide layer on the top of SiNWs surface and can be etched with HF. XRD analysis result (fig 1(d)) also proved that the resultant SiNWs are made up of silicon.

The as-synthesized samples appear black, which reveals the possibility of excellent optical anti-reflectance properties.

We find that by increasing the etching time, the less reflectivity can be obtained. The best reflectance is obtained at 80 min, and presents an effective reflectivity of 2.5 % (between 200 and 850nm) as shown in Figure 1 (e) . Reflectance value of our nanowires at different times ranging from 2.5 % to 3.85 % in the 200–850 nm wavelength range. Time dependant etching was performed to investigate the SiNWs growth rate and its mechanism.

Figure 2 shows the nanowires fabricated within 10, 30, 60 and 80 min respectively, while maintaining the solution concentration at 5.25 HF/0.02 AgNO<sub>3</sub> and temperature at 50 C.

Vertically aligned SiNWs arrays can be obviously seen in all images. The variation of the SiNWs length with etching time is shown in Fig 2 (f), indicates that SiNWs length increased linearly with etching time up to 1.5 h due to rapidity growth effect (17) . The average etching rate was estimated to be 36 nm min<sup>-1</sup>. It is believed that this low growth rate\_ comparing with pervious works (18) \_ is more related to the low resistivity of our starting silicon wafer around 0.01Ωcm(19) . Any way our results confirm that obtaining SiNWs with desired length can be achieved by controlling the etching time.

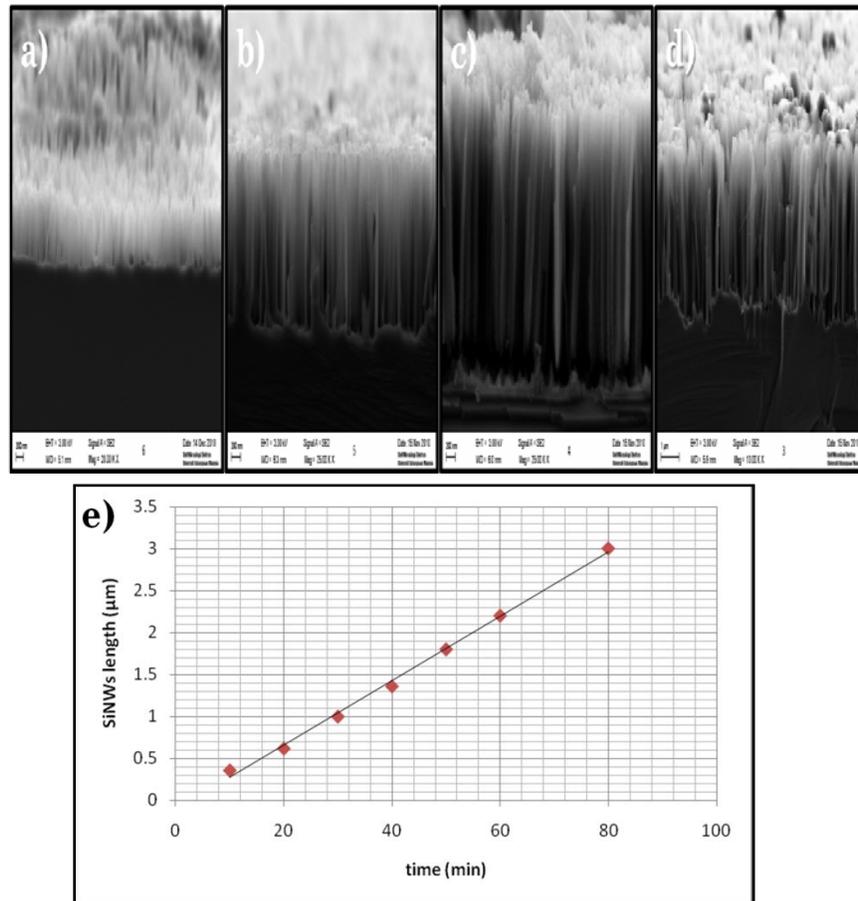


Fig. 2 cross-sectional SEM images of SiNWs prepared by metal-assisted wet-chemical etching in HF/AgNO<sub>3</sub> ( 5.25M/0.02M) at 50°C for different durations . a).10min. b). 30 min c). 60 min. d). 80 min. e). Silicon nanowires length as a function of etching time.

In order to study the effect of etching temperature on the formation processes of SiNWs, several samples were etched at different temperature in the range ( 25-100C), in addition to other common parameters were also fixed. SEM images of the samples are shown in Fig 3. a-d. The nanowire length as a function of a solution temperature was plotted as in Fig. 3. Fig 3(e) depicts that SiNWs length is

linearly proportional to the solution temperature in ( 25-100°C), which can be explained by the effect of the temperature gradient causing thermoelectric force and more electrons to be removed from the inside of silicon to the surface accelerating silver nano particles formation on silicon surface ( 20).

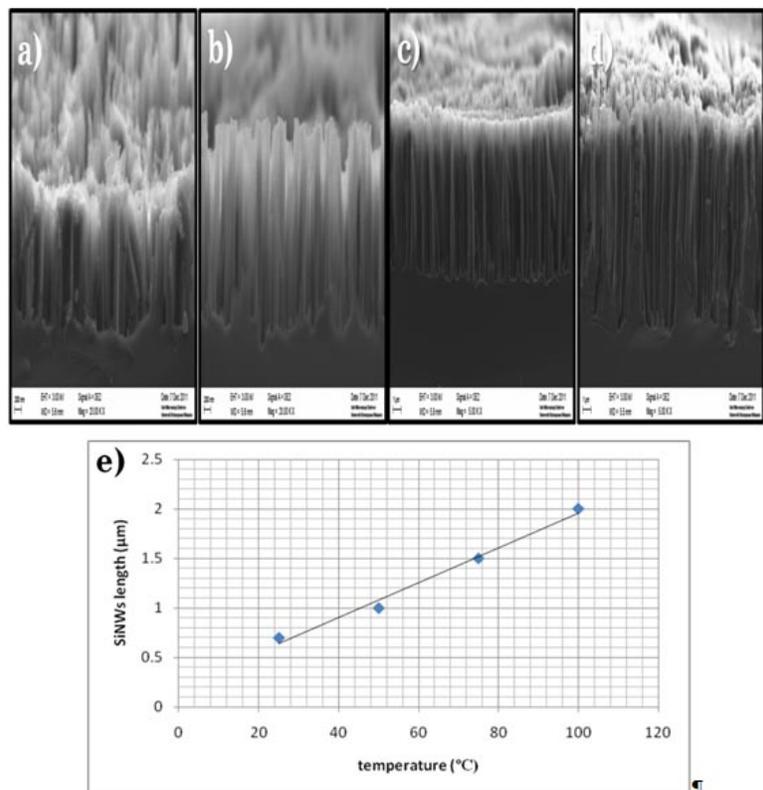


Fig. 3 cross-sectional SEM images of SiNWs prepared by metal-assisted wet-chemical etching in HF/AgNO<sub>3</sub> ( 5.25M/0.02M) for 30 min at different temperatures . a).25°C. b). 50 °C c). 75 °C. d). 100 °C e). Silicon nanowires length as a function of etching temperature.

In contrast to previous studies (21 ), our highly temperature etched silicon nanowires have not stuck to each other, however they look well aligned distributed uniformly over the whole silicon surface, refers to Fig. 3 . This result can be attributed to two reasons, firstly: the short period the silicon wafer goes through etching ( 30 min) that means short SiNWs.

The second reason and the major one is the high doping of the silicon wafer, whereas the amount of silver deposited on the surface is inversely proportional to the dopant concentration (19 ) .In conclusion, etching temperature was proved to be one of the effective methods to control the length of nanowires.

Under normal condition, the morphology of the SiNWs dramatically depends on HF and AgNO<sub>3</sub> concentrations. We have investigated here the effect of the solution concentration by reducing and increasing the concentration of AgNO<sub>3</sub> and HF one at a time. This way is to optimize the best growth parameters for p<sup>+</sup> SiNWs.

Figure 4 illustrates the influence of the concentration of the AgNO<sub>3</sub> upon SiNWs morphology. The concentration of the AgNO<sub>3</sub> employed are 0.015, 0,02, 0,035 and 0.05M, respectively. SiNWs were observed in the samples prepared with 0.015, 0.02 MAgNO<sub>3</sub> (fig 4). Increasing the concentration of AgNO<sub>3</sub> to more than 0.03 M, nanowires changed to porous microstructure.

This microstructure could be related to the increasing etching rate due to the increase of concentration. This hypothesis seems to be right as the silicon (nanowire/porous) length increases from 1 micron for 0.015M AgNO<sub>3</sub> to 5microns for 0.05 M concentration.

It is concluded that high concentration of AgNO<sub>3</sub> are not benefit for the SiNWs formation, and 0.015M-0.03M is acceptable range ofAgNO<sub>3</sub> concentration for vertical aligned SiNWs formation.

The concentration of HF can also affect SiNWs surface morphology. For the solution with 4.5, 5.25 M HF , silicon wafers were into vertical aligned SiNWs with different surface sharpness, just as shown in figures 5,. Increasing the concentration of HF to 5.5 , 7,10M as shown in figure 5 , we could see the porous like microstructure with increasing thickness.

So, the optimal growth parameters for SiNWs are ranging for AgNO<sub>3</sub> (0.015M -0.03M) , HF ( 4.5-5.25M). SEM plan observations reveal that the morphology does not significantly change with starting wafer resistivity changes of the from p<sup>+</sup> (0.01 Ωcm) to p<sup>-</sup> ( 10Ωcm) . For both 0.01 Ωcm and 10 Ωcm resistivity silicon, only vertical aligned SiNWs are formed. the depth of the nanowires increases with increasing resistivity.

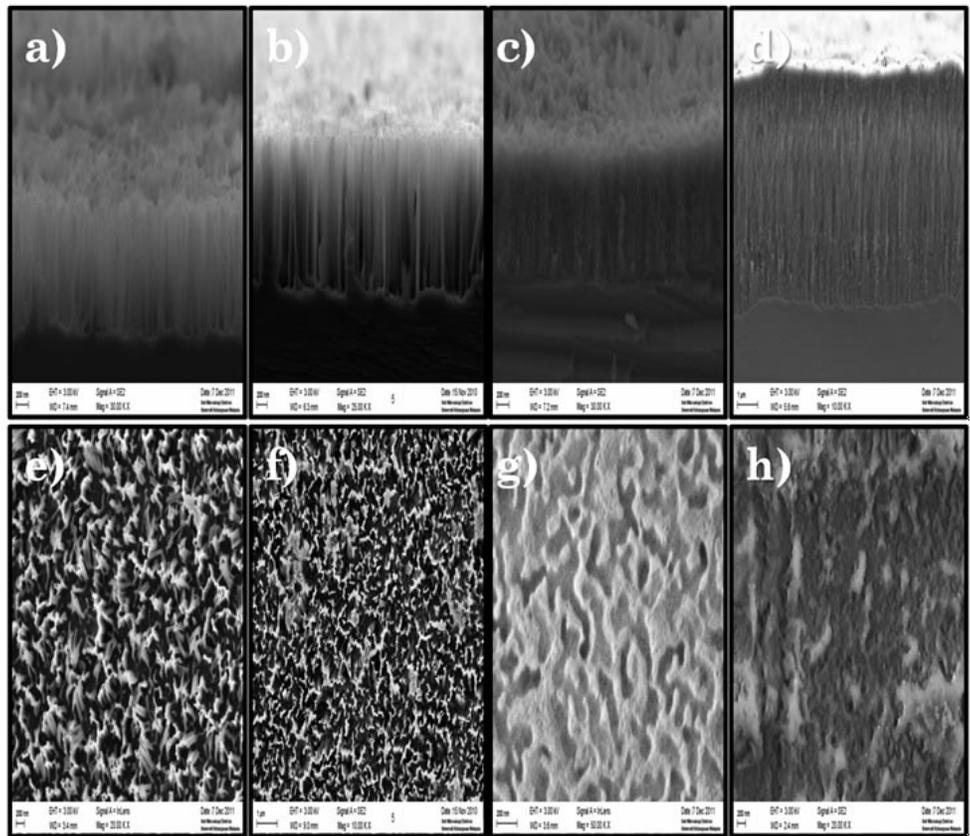


Fig. 4 Cross sectional and planer SEM images of SiNWs prepared by metal-assisted wet-chemical etching for 30 min at 50 °C in HF 5.25M and different concentration of AgNO<sub>3</sub>. a). & e). 0.015M . b). & f). 0.02M c). & g). 0.035M. d). & h). 0.05M

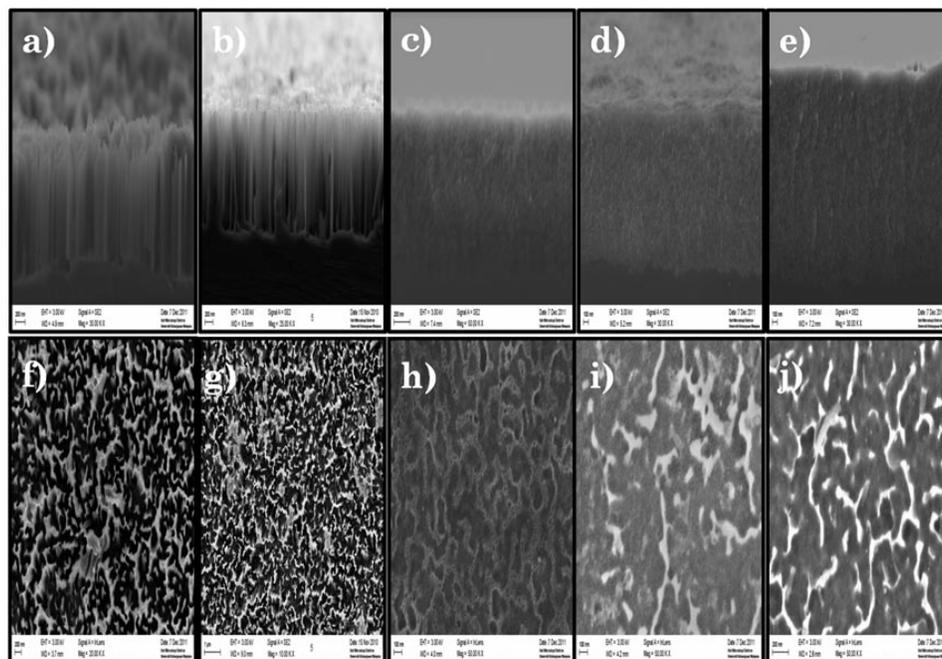


Fig. 5 cross-sectional and planer SEM images of SiNWs prepared by metal-assisted wet-chemical etching for 30 min at 50 °C in AgNO<sub>3</sub> 0.02M and different concentration of HF . a). & f). 4.5M . b). & g). 5.25 M c). & h). 5.5M d). & i). 7M e). & j). 10 M

So, the optimal growth parameters for SiNWs are ranging for AgNO<sub>3</sub> (0.015M -0.03M) , HF ( 4.5-5.25M). SEM plan observations reveal that the morphology does not significantly change with starting wafer resistivity changes of the from p+ (0.01 Ωcm) to p<sup>-</sup> ( 10Ωcm) . For both 0.01 Ωcm and 10 Ωcm resistivity silicon, only vertical aligned SiNWs are formed. the depth of the nanowires increases with increasing resistivity.

We find that the etching depth in p - (10 Ω cm) Si substrate is 2.5 times larger than that of p + (0.01 Ω cm) Si substrate, under identical conditions. This result is consistent with previous studies focused on silicon wafer resistivity effect on SiNWs formation (22). This behaviour may be attributed to the increase of the electron conduction band with silicon resistivity ( 23) .

Investigating other characteristics of the starting wafer like crystallographic orientation, doping density and type, our results revealed that The SiNWs possess the same type, same orientation and same doping level of the starting wafer (not shown here).

#### 4. CONCLUSION

The all of process conditions for the fabrication of Si NWs using the metal-assisted wet-chemical etching method have been studied in detail as a function of temperature, etching time, etching solution concentration and starting substrate characteristics. We find out that obtaining SiNWs with desired length can be achieved by controlling either the etching time or etching temperature, or both. The vertical aligned SiNWs structure was superior accomplished by the adjustment of etching solution concentration in specific ranges ( 0.015-0.03 M ) AgNO<sub>3</sub> and ( 4.5- 5.25 M ) HF.

Finally, our reflectivity results revealed that Si NWs fabricated over large areas with the metal-assisted wet-chemical etching method is a suitable antireflection coating for solar cell applications.

#### ACKNOWLEDGEMENT

The authors thank the Department of physics , and Solar Energy Institute, Universiti Kebangsaan Malaysia,

Bangi for facilities as well as to Malaysian Government for funding this project.

#### REFERENCES

- [1] Y. Huang , X. Duan, Y Cui, L. J. Lauhon, K. Kim, C. M. Lieber, Science, 294(2001), 1313 -1317.
- [2] Y. Huang, X. Duan, C. M. Lieber, Small, 1(2005),142-147.
- [3] J. Goldberger , A. I. Hochbaum ,R. Fan and P. Yang , NanoLett. 6 (2006), 973-977.
- [4] J. Bae , H. Kim, X. M. Zhang, C. H. Dang ,Y. Zhang, Y. J. Choi, A. Nurmikko ,Z. L.Wang , Nanotechnology, 21(2010) 095502, 1-5.
- [5] F. Qian , S. Gradedcak ,Y. Li, C. Y. Wen and C. M. Lieber, Nano Lett, 5( 2005), 2287-2291.
- [6] S. Huia, J. Zhang , X. Chena, H. Xua, D. Maa, Y. Liua and Bairui Taoa, Sensors and Actuators B: Chemical, 155(2011) , 592-597.
- [7] R, J. Y. Jung , Z. Guo, S.W. Jee, H.D.Um, K.-T. Park, J.H. Lee, Nanotechnology (IEEE-NANO),47 (2010), 1166-1172.
- [8] A. I. Boukai, Y. Bunimovich , J.Tahir-Kheli ,J.K. Yu, W.A. Goddard, J.R. Heath, Nature ,451(2008), 168-171.
- [9] D. Kumar, S. K. Srivastava, P.K. Singh, M. Husain, V. Kumar, Solar Energy Materials and Solar Cells, 95 (2011),215-218.
- [10] M. K. Sunkara, S. Sharma, R. Miranda, Applied Physics Letters , 79 (2001), 1546-1548.
- [11] Y. F. Zhang, Y. F. Tang, N. Wang, C. S. Lee, I. Bello, S. T. Lee, Appl. Phys. Lett. 72(1998), 1835-1837.
- [12] J. Niu, J. Sha, D. Yang, Physica E: Low-dimensional Systems and Nanostructures, 23 (2004), 1-2.
- [13] J. Mart , R. Garcia ,Nanotechnology, 21 (2010),245301.
- [14] Y. Q. Fu, A. Colli, A. Fasoli, J. K. Luo, A. J. Flewitt, A. C. Ferrari ,W. I. Milne, J. Vac. Sci. Technol. B, 27(2009), 1520-1526.
- [15] K. Peng, Y. Xu, Y. Wu, Y. Yan, S. T. Lee, J.Zhu, small, 11( 2005),1062-1067.
- [16] Z. Huang, X. Zhang, M. Reiche, L. Liu, W. Lee, T. Shimizu, S. Senz, U. Go` sele, NanoLett., 8(2008), 3046-3051.
- [17] . Li, R. Jia, C. Chen, Z. Xing, W. Ding, Y. Meng, D. Wu, X. Liu, T. Ye, Applied Physics Letters , 98 (2011), 151116.
- [18] D. Kumar, S. K. Srivastava, P.K. Singh, M. Husain, V. Kumar, J Nanopart Res, 12 ( 2010), 2267-2276.
- [19] X. Zong, Y. Qu, Y. C. Lin, L. Liao, X. Duan, Applied Material & Interfaces , 3(2011), 361-366.
- [20] Y. Liu, J. Zhang, Applied Mechanics and Materials, 138 (2012), 1082-1088.
- [21] K. Q. Peng, Y. J. Lan , S. P. Gao, J. Zhu, Advanced Material L,14 ( 2002), 1164-1167.
- [22] S. Cruz, A.H. Orville, J. Muller, J Electrochem. Soc., 152(2005), 4118.
- [23] Q. Fellahi, T. Hadjersi, M. Maamache, S. Bouanik, A. Manseri, Applied Surface Science, 257( 2010), 591-595.