

## Short Communication

# Area Effect of Reflectance in Silicon Nanowires Grown by Electroless Etching

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### **Abstract**

*This paper shows that the reflectance in silicon nanowires (SiNWs) can be optimized as a function of the area of silicon substrate where the nanostructure growth. SiNWs were fabricated over four different areas of silicon substrates to study the size effects using electroless etching technique. Three different etching solution concentrations of silver nitrate ( $\text{AgNO}_3$ ) and hydrofluoric acid (HF) at room temperature were used in the electroless etching process. Experiments showed that the reflectance in SiNWs can be decreased when the concentration of silver nitrate was optimized for a determinate size of silicon substrate.*

**Keywords:** Electroless metal deposition, Optical reflectance, Silicon nanowires.

## **1. INTRODUCTION**

SiNWs have attracted considerable attention for the past two decades due to the remarkable chemical and physical properties [1-3]. The application of SiNWs in solar cells is particularly interesting [4-7]. Studies suggest that silicon nanowires have a great potential to be utilized in photon absorption for solar cells due to the low optical reflectance in SiNWs at certain visible wavelengths.

There are a variety of techniques that have been used to fabricate Si nanostructures including electroless etching [8-16]. The electroless etching technique offers a simple and low cost mechanism to prepare long and large-area SiNW. Velez et al. [17] has recently reported very low optical reflectance in SiNWs using electroless etching technique. In their technique, the electroless etching was performed using three solution concentrations in an established size of silicon substrate during the initial process of preparation. Subsequently, this was followed by an un-stirred post cleaning

etching process using a nitric acid solution to remove silver dendrites from the monocrystalline silicon wafers [18].

Previously no studies have been reported on the substrate area effects on the reflectance properties of SiNWs. In this study, the optical reflectance in SiNWs as a function of both etching solution concentration and size of the silicon wafers are reported. Three different etching solution concentrations were used to grow SiNWs using four different sizes of the silicon substrates.

## **2. EXPERIMENTAL PROCEDURE**

A 1000 class clean room was used to fabricate SiNWs at room temperature by the electroless etching technique on one side polished single crystal p-type Si (100) wafers with resistivity of 10  $\Omega$ -cm. Four different area substrates of silicon wafers cut prepared ranging from 2, 4, 8 and 16  $\text{cm}^2$ . The Si wafers were cleaned using acetone, methanol and DI water to remove organic deposits from the surface of the

substrate. Buffered oxide etch (BOE) was used on the substrates for three minutes to remove surface native silicon dioxide grown during the cleaning process.

A concentration of 0.1 M silver nitrate ( $\text{AgNO}_3$ ) and 49% hydrofluoric acid (HF) diluted in DI water was used to prepare three different etching solution ratios in plastic petri dishes as presented in Table 1. The etching process of the cleaned Si wafers to obtain vertically aligned SiNW arrays was performed at room temperature for 30 minutes. After etching, each sample was dipped in two baths of 40 ml of DI water for 2 minutes to stop the etching process. From there samples were dipped in a concentrated nitric acid ( $\text{HNO}_3$ ) solution (20ml of DI water and 5ml of  $\text{HNO}_3$ ) for 30 min to completely remove the silver dendrites formed over the SiNWs [19]. Subsequently they were rinsed in DI water, and dried with nitrogen ( $\text{N}_2$ ).

A HITACHIS-4700 scanning electron microscope (SEM) was used to take the cross-sectional images of the cleaved SiNWs samples. A Varian Cary 100 UV–vis spectrophotometer was used in the visible region (350–800 nm) for reflectance analysis.

**Table 1.** Concentrations of Etching Solutions.

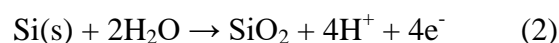
Solution	DI H <sub>2</sub> O (% Vol.,ml)	AgNO <sub>3</sub> (% Vol.,ml)	HF (% Vol.,ml)
1	60, 18	13.33, 4	26.66, 8
2	60, 18	16.66, 5	23.33, 7
3	60, 18	20, 6	20, 6

### 3. RESULTADOS AND DISCUSSION

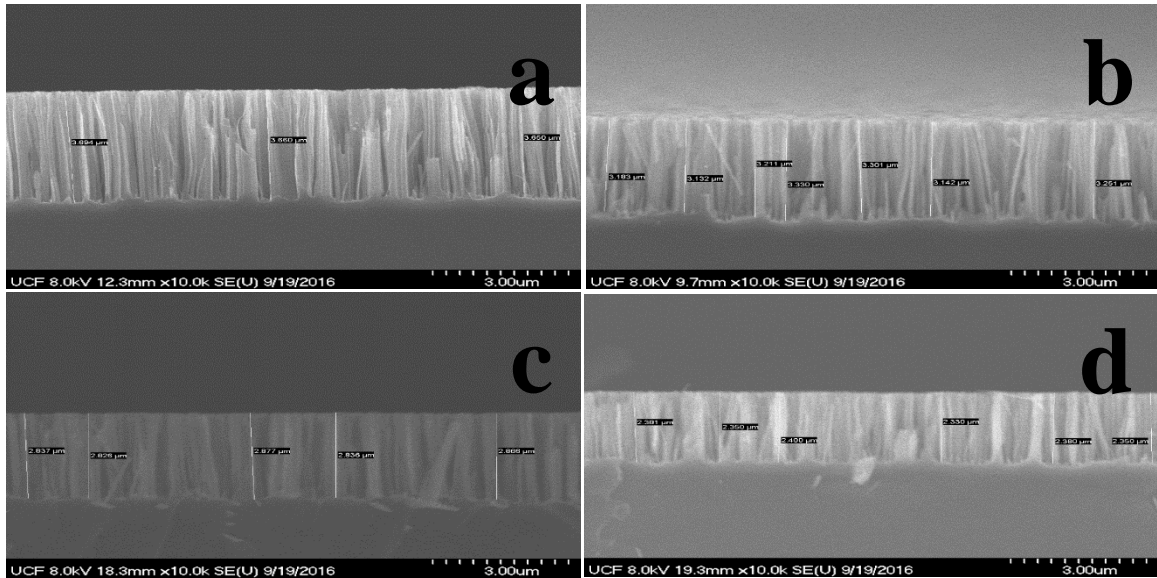
The cross-sectional SEM images presented in figures 1(a)–(d), 2(a)–(d) and 3(a)–(d) respectively shown SiNW arrays prepared by using three concentrations on four different sizes of silicon substrates. It can be seen from these figures that the lengths of the SiNWs change with the concentration of HF and  $\text{AgNO}_3$  and the size of silicon substrate where the nanostructures are prepared. Digital images of measurements of the SiNWs

lengths were acquired and processed by software (QUARTZ PCI) that came with HITACHIS-4700.

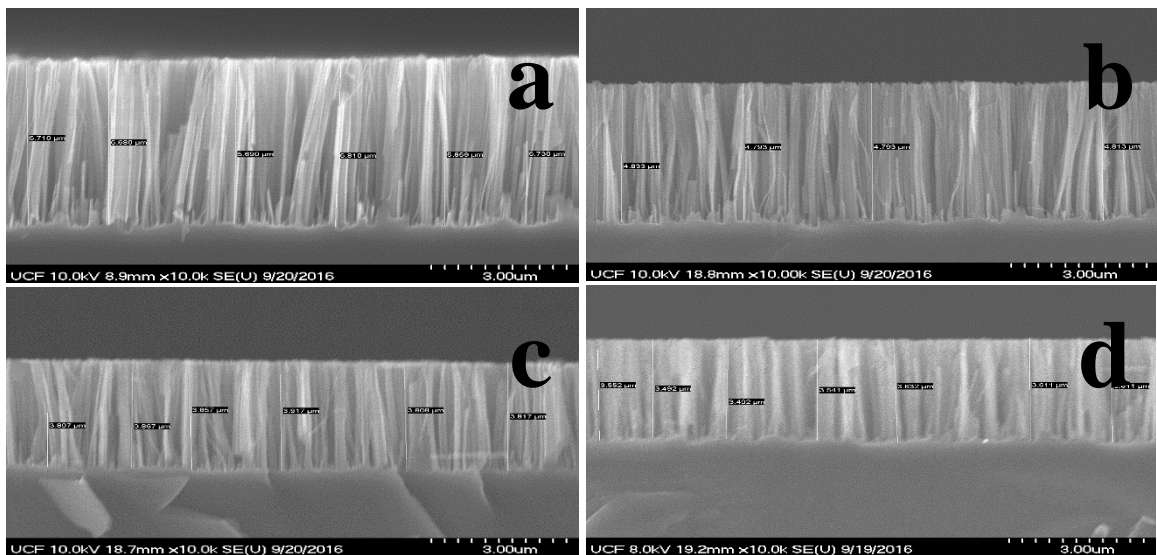
Figure 4 shows the effect of  $\text{AgNO}_3$  and HF concentration ratios on the length of SiNW arrays for different wafer surface sizes. The length of the SiNWs increases with the increase in  $\text{AgNO}_3$  concentration in the etching solution. Taller SiNWs can be achieved with smaller areas of wafer surface. When any of the precursors is depleted the etching process ceases for a determined substrate size, in spite of that, the silver is depleted most rapidly in the solution in larger sizes of silicon substrates, because four atoms of silver are necessary to release a single atom of Si [20]. If the solution or the silicon wafer surface size is substantially changed then one of the other precursors will run out before. In the reaction of four atoms of silver, six fluorine atoms combine with a single atom of Si [21]. It means that as seen in the following reactions:



In this Si/ $\text{AgNO}_3$ /HF combination occurs a corrosion-redox reaction. Initially,  $\text{Ag}^+$  ions capture electrons from the valence band of Si reducing the  $\text{Ag}^+$  ions and oxidizing the silicon where Ag deposits. Ag particles are formed due to this reaction and  $\text{SiO}_2$  is produced underneath of them. The etching of  $\text{SiO}_2$  by the HF solution forms vertical shallow pits below the Ag particles resulting in silicon nanowires. The dependency of Si NW length falls on etching duration, temperature and solution concentration. However, a detailed and wide range parametric study that enables full control over Si NW length and distribution is missing [22]. Therefore, choosing the right concentration ratio is necessary to achieve lengthy grown SiNWs. Longer and straight nanowires are



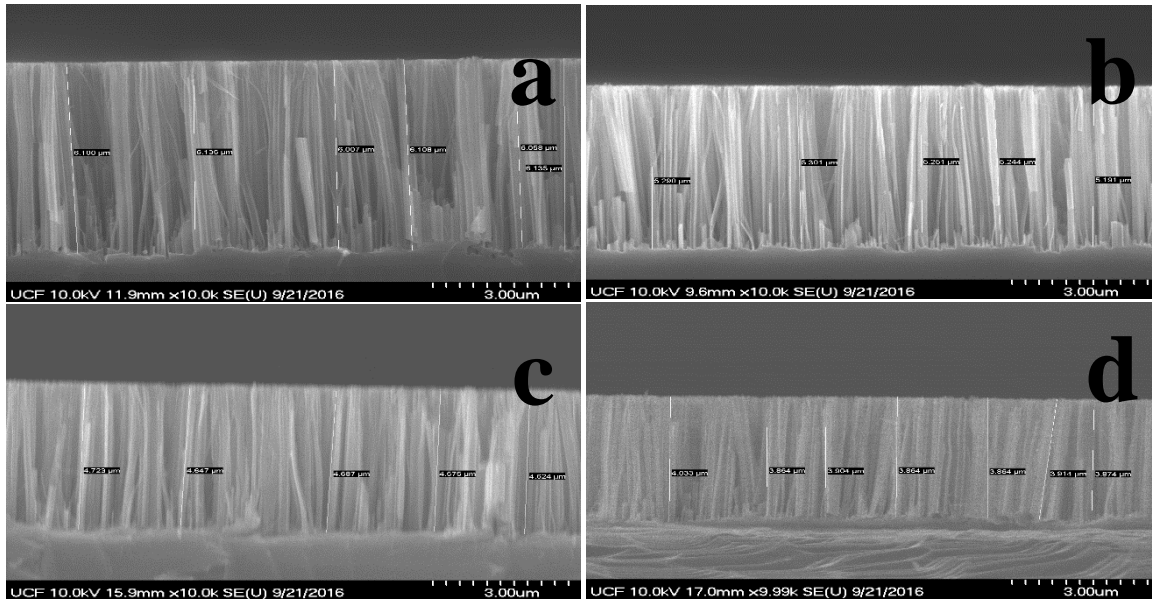
**Figure 1.** SEM pictures of the SiNWs grown using the concentration of HF 26.666 % and  $\text{AgNO}_3$  13.334 % grown in a silicon wafer size surface of (a)  $2 \text{ cm}^2$  (b)  $4 \text{ cm}^2$  (c)  $8 \text{ cm}^2$  and (d)  $16 \text{ cm}^2$ .



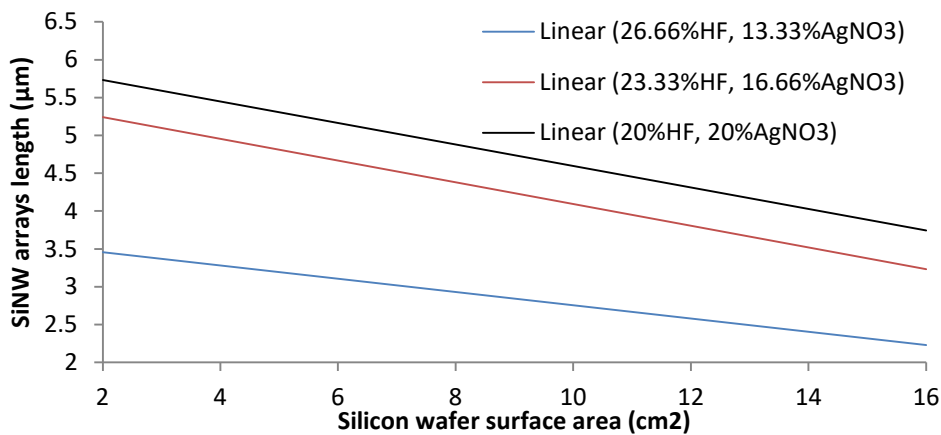
**Figure 2.** SEM pictures of the SiNWs grown using the concentration of HF 23.33 % and  $\text{AgNO}_3$  16.66 % grown in a silicon wafer size surface of (a)  $2 \text{ cm}^2$  (b)  $4 \text{ cm}^2$  (c)  $8 \text{ cm}^2$  and (d)  $16 \text{ cm}^2$ .

desired due to the formation of high density and uniform distributed arrays. These features shape a strong light trapping structure in the SiNWs proving lower reflective performance. However, an early depletion of silver in the concentration will decrease the reaction kinetics due to the considerable amount of atoms of Ag necessary to combine with a single atom of Si. This reduction of Ag

will lead to cease the sinking mechanism of  $\text{Ag}^+$  ions towards the bottom of the nanostructures stopping the growth of SiNWs. Therefore, termination of the growing process of SiNWs will affect the light trapping properties of the nanostructures decreasing their antireflection performance.



**Figure 3.** SEM pictures of the SiNWs grown using the concentration of HF 20 % and AgNO<sub>3</sub> 20 % grown in a silicon wafer size surface of (a) 2 cm<sup>2</sup> (b) 4 cm<sup>2</sup> (c) 8 cm<sup>2</sup> and (d) 16 cm<sup>2</sup>.



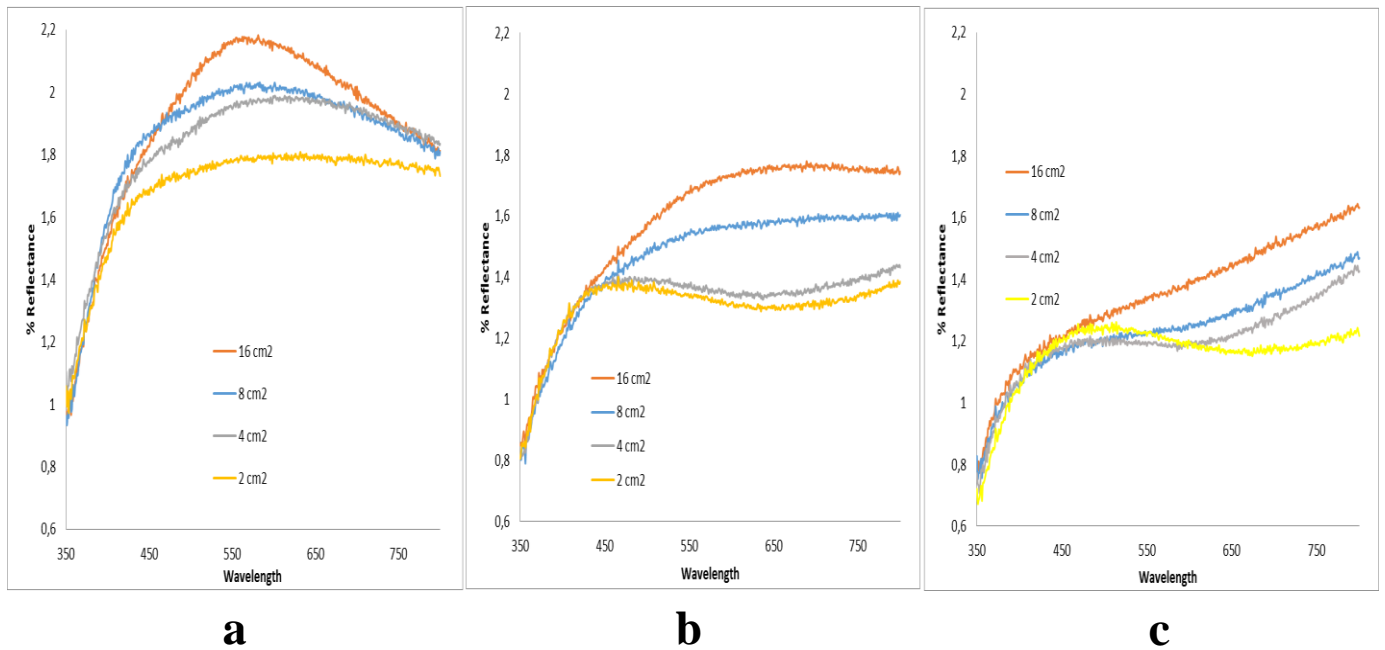
**Figure 4.** SiNW arrays length as a function of silicon surface areas for different etching solution concentrations.

Similarly, an increase of reflectance in SiNWs may be obtained if the area exposed to the electroless etching is increased maintaining the same concentration of the solution due the necessary atoms of Ag for the reaction.

The percentage of HF in the solution and the total area of Si etched determine the depletion rate of silver. The most predominant wavelengths in the solar

spectrum at air-mass 1.5 [23] are in the range from 350–850 nm. The reflectance plots of the samples are shown in Figures 5(a)–(c).

It can be seen from these figures that when we increase the concentration of AgNO<sub>3</sub> and reduce the wafer surface size, the reflectance in SiNWs is lower for the wavelengths where predominant the solar radiation spectrum.



**Figure 5.** Reflectance plots of SiNWs prepared with different substrate surface sizes (2, 4, 8 and 16 cm<sup>2</sup>) for varies concentrations of, (a) HF is 26.66% and AgNO<sub>3</sub> is 13.33%, (b) HF is 23.33% and AgNO<sub>3</sub> is 16.66% and (c) HF is 20% and AgNO<sub>3</sub> is 20%.

#### 4. CONCLUSION

SiNWs prepared by electroless etching method can significantly increase light absorption abroad the solar light spectrum. Lower reflectance in the samples is produced when AgNO<sub>3</sub> is increased in the etching solution. A lower reflectance in SiNWs is achieved when the silicon substrate size is reduced. However, an optimum concentration of 20% HF and 20% AgNO<sub>3</sub> in the etching solution produces the best absorption in SiNWs for the smaller area studied in this experiment,

2 cm<sup>2</sup>, and wavelengths greater than 600nm. In order to achieve lower reflectance performance in SiNW arrays, solution concentrations of HF and AgNO<sub>3</sub> and the size of the samples must be controlled during the SiNWs growth.

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