Nanostructure, Optical and Optoelectronic Properties of Silver Nanoparticle-based Chemical Etching on Monocrystalline Silicon for Solar Cell Applications

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Abstract: Introduction: Silver nanoparticle (AgNP)-based chemical etching is applied to produce silicon nanowires (SiNWs) on monocrystalline silicon.

Background: Development of silicon nanowires (SiNWs) for various applications has seen a significant leap in recent years. These nanowires are privileged for their outstanding properties in a wide variety of applications. Indeed, numerous potential applications have been devised which rely on SiNWs, including opto-electronics, photovoltaic and biomedical [1-3].

A nanoscale mask is commonly used to produce silicon nanostructures using the dry etching method [4, 5]. This technique damages silicon structure and morphology owing to the use of high ion energy [6]; in addition, this approach is complicated and expensive. More recently, other interesting techniques such as surface plasmon resonance (SPR) were demonstrated as potential effective methods for improving surface properties and their applications [7-13]. In other works, silver nanoparticle (AgNPs)-based chemical etching constitutes an excellent method that can be used to produce monocrystalline silicon nanowires (SiNWs) for optical and optoelectronic devices [14-16]. This approach has a simple procedure, allows fast fabrication, has lower cost, and is a high throughput technical solution for fabricating various SiNWs. These are customarily formed by the metal-assisted chemical etching method and are mainly based on two protocols: (i) the deposition of metal particles and (ii) the etching of silicon [17].

The optical and optoelectronic properties of SiNWs are strongly correlated with chemical etching time, acid concentration, and solution temperature of AgNPs. Good efficiency (12%) is reached for vertical SiNWs that are used in a radial p-i-n structure [18]. Similarly, an improvement in solar cells that are based on SiNWs has been noted by Rosaria et al. [19]. In this study, the electronic quality of silicon after nanowire formation was studied. The effect of monocrystalline SiNWs passivation by stain etching treatment on morphology, optical, and optoelectronic properties was investigated and applied to solar cell-based SiNWs.

1. INTRODUCTION

Keywords: Monocrystalline silicon, nanowires, etching, recombination velocity, silicon solar cell.

2. EXPERIMENTAL

The process used to produce SiNWs is shown in Fig. (1). In this process, a 1.6 × 1.6 cm² monocrystalline silicon substrate, with p-type (100) orientation and 0.1–0.2 × 10⁻¹ Ω.cm resistivity, was employed. The SiNWs production process consists of four steps. (i) The first step starts by rinsing silicon substrate in an HF/H₂O/AgNO₃ solution containing 0
mL of HF, 90 mL of H₂O₂, and 0.17 g of AgNO₃. This process leads to the deposition of AgNPs on the surface of the substrate. (ii) In the second step, silicon wafer covered by metallic silver is immersed in an HF/H₂O₂/H₂O solution (10 mL of 48-wt% HF/1 mL of 30-wt% H₂O₂/40 mL of H₂O). During this step, AgNPs are oxidized and disperse in the HF solution. During this process, AgNPs etch into the silicon substrate, which produces SiNWs [20, 21]; various nanowire lengths are obtained by changing the etching time. (iii) The third step consists of eliminating residual AgNPs located at the bottom of nanowires by simple etching in a dilute HNO₃ solution. (iv) The final step is known as the passivation stage. During this step, SiNWs are immersed in an HNO₃/H₂O/HF solution for 15 s.

![Fig. (1)](image)

**Fig. (1).** Steps to produce SiNWs: (I) Deposition of AgNPs on silicon surface in HF/H₂O/AgNO₃, (II) generation of holes via silicon oxidation by HF, (III) formation of SiNWs arrays, (IV) removal of residual AgNPs from nanowires by an HNO₃ solution. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

The morphologies, optical and optoelectronic properties of the obtained nanowires were investigated as a function of etching time. During the reaction between Si and AgNO₃, the appearance of black color is observed. A similar effect was also observed by Martin *et al.* [22]. The morphologies of SiNWs as a function of etching time were measured using scanning electron microscopy (SEM). The total reflectivity of produced SiNWs was estimated by a spectrophotometer (PerkinElmer Lambda 950) equipped with an integrating sphere operating in the 300–1100 nm wavelength range. Finally, effective lifetimes were determined by photoconductance measurements (model WCT-120 Silicon Wafer Lifetime Tester).

3. RESULTS AND DISCUSSION

The SEM cross-sections of produced nanowire samples are shown in Fig. (2). The obtained SiNWs cross-sections clearly show that the length of SiNWs is proportional to etching time (tₑ) [see step number (ii)]. The obtained structures are suitable for light trapping inside SiNWs. Silicon type affects nanowire length; this occurs because the doping concentration of silicon substrate causes defects and impurities, which leads to pore formation and affect SiNWs length [23-25].

Total reflectivity before and after SiNWs formation is shown in Fig. (3). This figure shows considerable differences in reflections; specifically, after 20 min of etching, reflectivity decreases from 38% for nanowire length (Lₙ) of 0 µm to 1% for a Lₙ of 10 µm and 20% after 40 min of etching for Lₙ of 3 µm. These results are comparable to those for SiNₓ [26, 27] and much better than those for mechanically textured [28] (produced 12% reflection) and NaOH and KOH wet texturization-processed silicon [28-29] (produced 18% reflection). A decrease in reflectivity owing to the significant internal surface area of SiNWs and reflections between the rays lead to light confinement. The characteristic diameter of SiNWs and the distance between wires result in low reflection in the visible wavelength range [30, 31]. The result obtained using a simple method makes SiNWs very promising for photonics, optical, and photovoltaic applications [32]. Fig. 4 shows the correlation between nanowire lengths and reflectivity at 700 nm. After the fabrication process, the electronic properties of SiNWs before and after passivation were investigated. Variations in the effective lifetime (τₑ) and surface velocity recombination (Sₑ) are summarized in Table 1. Equation 1 [33] was used to extract the value of Sₑ from the effective carrier lifetime τₑ:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{2S_{\text{eff}}}{W}
\]

(Eq. 1)

where τₙ is the bulk lifetime, and W is the sample thickness. For high values of τₑ, the term 1/τₙ may be neglected. Therefore, the effective recombination surface is obtained using Eq. (2):

\[
S_{\text{eff, Max}} = \frac{W}{2\tau_{\text{eff}}}
\]

(Eq. 2)

![Fig. (2)](image)

**Fig. (2).** Effect of etching time on the length of obtained SiNWs [(a) 20 min and (b) 40 min]. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

Table 1 shows the measured values of τₑ and Sₑ before and after SiNWs passivation. Measurements of lifetime were made according to Yuan-Fong Chou Chau *et al.* [34].

It is observed that the value of SiNWs lifetimes of approximately 0.8 µs is low compared to that of the bare substrate (1 µs), and the value increases after passivation to approximately 10 µs. Concurrently, SiNWs production can generate defects in the silicon surface. When the number of surface defects increased, the recombination of generated minority carriers also became more significant, which
prompted a decrease in \( \tau_{\text{eff}} \) from 1 \( \mu \text{s} \) for the bare sample to 0.8 \( \mu \text{s} \) for the SiNWs sample. This lower lifetime is due to excess AgNPs, which act as recombination centers [35].

**Table 1. Lifetime \( (\tau_{\text{eff}}) \) and recombination velocity \( (S_{\text{eff}}) \) of optimized SiNWs before and after passivation.**

<table>
<thead>
<tr>
<th>-</th>
<th>Ref. silicon</th>
<th>SiNWs</th>
<th>Passivated SiNWs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{\text{eff}} ) (( \mu \text{s} ))</td>
<td>1.0</td>
<td>0.8</td>
<td>10.0</td>
</tr>
<tr>
<td>( S_{\text{eff}} ) (cm.s(^{-1}))</td>
<td>165</td>
<td>206</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Consequently, \( S_{\text{eff}} \) increases from 165 to 206 cm.s\(^{-1}\) for the bare sample and after SiNWs formation, respectively. A considerable improvement in the electronic quality of the sample after SiNWs passivation by the stain etching method was observed. As a result, an enhancement of \( \tau_{\text{eff}} \) (exceeds 10 \( \mu \text{s} \) after passivation for 120 s), which is characterized by a decrease in \( S_{\text{eff}} \) (i.e., 16.5 cm.s\(^{-1}\)), leads to the reduction in surface recombination (surface passivation by H and O bonds) [36-38]. This characteristic is essential for high efficiency silicon solar cells.

For the fabrication of silicon solar cells, a monocrystalline silicon p-type boron-doped (100) orientation with a surface area of 1.6 \( \times \) 1.6 cm\(^2\), the thickness of 330 \( \mu \text{m} \), and resistivity of 0.01–0.02 \( \Omega \text{cm} \) was used. The junction (formation of the \( n^+/p \) structure) was realized by phosphorus diffusion on the front surface using the spinning method in the furnace at 925°C for 30 min. Thermally evaporated aluminum was used for front and back contacts. The front surface of SiNWs areas was coated using a special mask. The graphs of current versus voltage of solar cells based on SiNWs before and after passivation are shown in Fig. 4. By comparing cells before and after passivation, an improvement in the current density \( (J) \) and the solar energy conversion efficiency \( (\eta) \) values was achieved; the obtained values were approximately 26.9 mA.cm\(^{-2}\) and 15% (i.e., 77.5% improvement), respectively. An improvement in the efficiency \( (\eta) \) value (The portion of energy in the form of sunlight that can be converted via photovoltaics into electricity by the solar cell) is attributed to surface recombination reduction, which is referred to as the passivation effect [39-42].

**Fig. (3).** Total reflectivity as a function of wavelength at different etching time (0,20, and 40 min), respectively. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

**Fig. (4).** Current–voltage characteristics of SiNWs-based solar cells before and after passivation under AM1.5. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

**Table 2. Electrical parameters of the SiNWs-based solar cell compared to an untreated solar cell.**

<table>
<thead>
<tr>
<th>Electrical Parameters</th>
<th>Untreated Solar Cell</th>
<th>Passivated SiNWs Solar Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J ) (mA/cm(^2))</td>
<td>20.5</td>
<td>26.9</td>
</tr>
<tr>
<td>( \text{Voc} ) (V)</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>FF (%)</td>
<td>65</td>
<td>78</td>
</tr>
<tr>
<td>( \eta ) (%)</td>
<td>9</td>
<td>15.2</td>
</tr>
</tbody>
</table>

The current density and fill factor (FF) improvement observed after SiNWs passivation (see Table 2) resulted in improved efficiency \( (\eta) \) of the SiNWs-based solar cell, and increased from 9% to 15%. This efficiency improvement is explained by two simultaneous phenomena, i.e., the antireflection phenomena of the SiNWs layer and the passivation of the SiNWs surface [43-45].

**CONCLUSION**

In this study, the structural, optical, and optoelectronic properties of SiNWs were investigated as a function of etching time for the AgNPs method. SiNWs fabricated using optimum conditions revealed low reflection of approximately 1% in the wavelength range of 300–1100 nm compared to those produced by other methods such as texturization by KOH and mechanical means (i.e., reflectivity of 12–18%). The achieved desirable anti-reflectivity by SiNWs is highly recommended for high-efficiency monocrystalline silicon solar cells. The enhancement in conversion efficiency from 9% to 15% after the passivation process using a simple and inexpensive production process shows that it is possible to produce highly efficient SiNWs-based solar cells.
LIST OF ABBREVIATIONS

AgNPs = Silver nanoparticles
S_eff = Surface recombination velocity
t_eff = Effective lifetime
SiNWs = Silicon nanowires
t_et = Etching time
SEM = Scanning electron microscopy
J = current density
η = solar energy conversion efficiency
FF = Fill factor

ETHICS APPROVAL AND CONSENT TO PARTICIPE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

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