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Etching time effect on optical properties of porous silicon for solar cells fabrication

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\textbf{A B S T R A C T}

The dependence of porous silicon (PS) morphology on fabrication conditions using electrochemical etching (ECE) was investigated. The porosity of the material is determined by gravimetric analysis. The effect of various etching time: 30, 60, and 120 min with a constant DC current density of 5 mA/cm\textsuperscript{2}, on structural and optical properties of PS has been studied. The optical properties such as reflectivity, energetic transition, and refractive index were analyzed by using specific models. Photoluminescence spectroscopy (PL) was conducted to elaborate the energy gap of PS. UV–vis spectrometry was used to study the optical properties of processed samples with various percentage porosity: 9.47%, 33.39%, and 63.93%. The obtained results are in good agreement with both theoretical and experimental data.

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1. Introduction

Research grade silicon substrate is made of high quality single crystal with very low density of impurities and controlled amount of dopants. It can be prepared with flat atomic scale by standard methods that lead to porous silicon (PS) formation under a specific process \cite{1}. This material many interesting characteristics such as direct and wide modulated energy band gap \cite{2,3}. It is observed to form in the electro-polishing experiments using an electrolyte solution comprising hydrofluoric acid \cite{4}. The high surface area of PS is found to represent a useful model for crystalline silicon surfaces in spectroscopic studies \cite{5–7}. Accordingly, successful experiments have discovered that electrochemical and chemical dissolution enable the silicon (Si) wafers to emit light in red luminescence \cite{8}. During the last two decades, the optical properties of PS have become a very intense area of research.

Al-Douri et al. \cite{9} have calculated using an empirical pseudopotential method (EPM), the energy gap of Si which is found to be indirect. They have investigated features such as refractive index, optical dielectric constant, bulk modulus, elastic constants and short-range force constants, in addition to the shear modulus, Young’s modulus, and Poisson’s ratio and Lame’s constants for both Si and PS. They have found that Debye temperature of PS can be estimated from the average sound velocity. While, Ramizy et al. \cite{10} have used electrochemical etching to fabricate PS surfaces on both sides of the Si wafer. They have looked at the effect of PS on the performance of Si solar cells and reflected mirrors, respectively. They also have shown that PS has discrete pores and short-branched pores on the polished wafer side. In contrast, the etched backside of

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the wafer has smaller pore size. They have reported an increase of the solar cell efficiency to 15.4% when PS is formed on both sides of the silicon wafer. Nanowires with dimensions of few nanometers were formed on the entire etched surface. The optical analysis of Si nanostructures was studied by Omar et al. [11]. They have observed a blue shift luminescence at 660 nm and 629 nm for PS made by electrochemical etching and by laser-induced etching, respectively. They have shown by using X-ray Diffraction (XRD) that the crystallites size of PS provides an estimated degree of crystallinity of the etched sample.

In this work, PS was fabricated using photoelectrochemical etching at different etching time and very low current to explore uniform PS. The optical properties of PS were studied to establish an appropriate refractive index model within specific time and percentage porosity for solar cells fabrication.

2. Experimental procedure

The n-type Si (100) wafer is used with resistivity of 0.75–1.25 Ω·cm and 2-in. diameter in size. The Si wafer was first cleaned using radio corporation of America method (RCA) cleaning procedure. Our experimental setup is shown in Fig. 1. The electrochemical cell is made of Teflon and has a circular aperture at the bottom with a radius of 10 mm, under which Si wafer is sealed. The cell has two electrodes: Si wafer is used as the anode electrode and platinum on top as the cathode electrode. The front side of Si wafer is in contact with HF: ethanol solution and the back side is attached to copper to make electrical contact. The uniformity of PS is obtained with the anodization cell that can be observed at first sight in Fig. 2, the etched area of the layers presents a uniform shape.

PS is formed by photoelectrochemical etching on n-type Si wafer by using a solution of HF: ethanol = 1:4 (in volume) under external illumination. The etching time of the electrochemical process is 30, 60, and 120 min under a constant current density of 5 mA/cm² DC. The etched Si sample was then rinsed in deionized water and dried with N₂ gas. The PS was made at different doping levels below 10¹⁸ cm⁻³ using an external light to generate positive charges “holes”. Under anodic potential and HF solution, the Si dissolves when holes are present. The samples were characterized by scanning electron microscope (SEM), (SEM Nova NanoSEM 450, USA) and analyzed by photoluminescence (PL), (Jobin Yvon model HR 800 UV system, USA) and UV–vis spectrophotometer, (Perkin Elmer Lambda 35, USA).

3. Results and discussion

Different mechanisms of Si dissolution have been presented. It is accepted that holes are required for pores formation. During this formation, two hydrogen atoms (H₂) are evolved for each dissolved Si atom [12,13]. Current efficiencies are about two electrons per dissolved Si atom during pores formation [13–15]. The final chemical reaction can be formulated as follows:

\[ \text{Si} + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_2 + 2\text{H} + +2\text{e}^- \]  

(1)
According to Beale et al. model [16], Schottky barrier can be created between the semiconductor and the electrolyte, where the Fermi level is occurring at the Si/electrolyte interface. The reduction of Schottky barrier height is attributed to the intensified electric field at dissolved pore tips.

SEM is very useful in evaluating the percentage of pores made by different fabrication methods, in combination with an image processing technique [17]. Our results are carried out using gravimetric method [18],

\[ P(\%) = \frac{m_1 - m_2}{m_1 - m_3} \times 100 \]  

where \( m_1 \) and \( m_2 \) correspond to the sample weights before and after etching process, respectively. Whereas, \( m_3 \) is the sample weight after removing the PS layer with 3\% KOH or 20\% NaOH solution.

Fig. 3(a) shows SEM image of PS at 30 min etching time and current density of 5 mA/cm\(^2\) DC. The surface of n-Si sample is crooked; pores were not evidently observed and porosity is low (9.47\%). Fig. 3(b) shows SEM image of PS backside at 60 min etching time. Pores exhibit randomly distributed (inhomogeneity) at a porosity percentage of 33.39\%. Fig. 3(c) shows a high resolution SEM image of PS formation after 120 min etching time. PS exhibits uniform and clear circular distribution of pores with highest porosity percentage of 63.93\%. A summary of the structural characteristic of PS at different etching time and constant current density is given in Table 1. As the etching time increases, the porosity increases at a fixed HF:ethanol ratio.

Fig. 4 shows direct correlation of porosity percentage with etching time. The effect of different etching times under a constant current density of 5 mA/cm\(^2\) and a fixed solution of HF: ethanol = 1:4 on PS is analyzed. At etching time of 30 min, the physical holes were not clearly noticed; these holes indicate the start of etching process on the silicon wafer. The surface of Si consists of discrete pores with short tunnels and smooth walls. By increasing the etching time to 60 min, the edges of the remaining non-etched layer were observed. This may be attributed to insufficient etching time to dissolve all chemically treated area. When etching time is increased to 120 min, the obtained pores became more homogeneous, this means that the higher density of electron-hole pairs at the semiconductor-electrolyte interface favors the dissolution of the remaining non-etched layer. Deeper and smaller pores appeared when the exposure time reached 120 min [19].

The photoluminescence (PL) response is shown in Fig. 5, where the intensity of PS increases as porosity percentage increases. It means that PL intensity is proportional to the number of secondary emitted photons in PS. The higher energy is
dominated by surface-state recombination and low energy emission originates from the quantum confinement effect [20]. Furthermore, the energy band gap \( E_g \) is calculated using:

\[
E_g = \frac{1240}{\lambda}
\]

where \( \lambda \) is the wavelength in (nm). The maximum PL intensity of PS shows blue shift at peak equals to 651.362 nm with \( E_g = 1.90 \text{ eV} \) for 120 min, 666.45 nm with \( E_g = 1.86 \text{ eV} \) for 60 min, and 662.985 nm with \( E_g = 1.83 \text{ eV} \) for 30 min. The band gap increases as the concentration of mobile charged carriers decreases within the remaining silicon structure of PS [21]. The highest obtained porosity percentage is 63.73\% as shown in Fig. 6. The etching time of 120 min resulted in a blue-shifted peak as shown in the reflection spectrum of PS at different porosity percentage (Fig. 7). This appears to be enough to break the bonding of Si atoms from the wafer during chemical reaction, making the porous region to expand during this etching.
Fig. 7. Reflection spectrum of PS of different porosity percentage.

Table 2
Reflectivity, energy gap, reflective index using Ravindra et al. [29], Herve and Vandamme [30] and Ghosh et al. [31] and optical dielectric constant of PS.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Reflectivity (%)</th>
<th>( E_g ) (eV)</th>
<th>n</th>
<th>( \varepsilon_{\infty} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As grown</td>
<td>74.14</td>
<td>1.12</td>
<td>3.353 (^{d})</td>
<td>11.242 (^{d})</td>
</tr>
<tr>
<td></td>
<td>60.45</td>
<td>1.11 (^{a,b})</td>
<td>3.170 (^{e})</td>
<td>10.048 (^{e})</td>
</tr>
<tr>
<td></td>
<td>53.77</td>
<td>1.11 (^{f})</td>
<td>3.451 (^{f})</td>
<td>11.909 (^{f})</td>
</tr>
<tr>
<td>30</td>
<td>16.29</td>
<td>1.83</td>
<td>2.913 (^{g})</td>
<td>8.485 (^{g})</td>
</tr>
<tr>
<td></td>
<td>30.92</td>
<td>2.786 (^{g})</td>
<td>8.386 (^{g})</td>
<td>7.761 (^{g})</td>
</tr>
<tr>
<td></td>
<td>42.43</td>
<td>2.896 (^{g})</td>
<td>8.386 (^{g})</td>
<td>7.761 (^{g})</td>
</tr>
<tr>
<td>60</td>
<td>13.83</td>
<td>1.86</td>
<td>2.8894 (^{d})</td>
<td>8.346 (^{d})</td>
</tr>
<tr>
<td></td>
<td>28.86</td>
<td>2.772 (^{e})</td>
<td>8.277 (^{e})</td>
<td>7.683 (^{e})</td>
</tr>
<tr>
<td></td>
<td>40.38</td>
<td>2.877 (^{e})</td>
<td>8.277 (^{e})</td>
<td>7.683 (^{e})</td>
</tr>
<tr>
<td>120</td>
<td>10.96</td>
<td>1.90</td>
<td>2.754 (^{f})</td>
<td>8.236 (^{d})</td>
</tr>
<tr>
<td></td>
<td>18.37</td>
<td>2.853 (^{f})</td>
<td>8.236 (^{d})</td>
<td>7.584 (^{f})</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>2.786 (^{f})</td>
<td>8.139 (^{f})</td>
<td>7.584 (^{f})</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. [40] theo.
\(^{b}\) Ref. [41] theo.
\(^{c}\) Ref. [9] exp.
\(^{d}\) Ref. [29].
\(^{e}\) Ref. [30].
\(^{f}\) Ref. [31].
\(^{g}\) Ref. [42,43] exp.
\(^{h}\) Ref. [44] exp.

This results in a thinner wall between the formed Si pores over a larger exposed area, thereby increasing the observed PL intensity [22].

The lowest effective reflectance was obtained from PS formed at 120 min. Therefore, the refractive index decreases as the porosity percentage increases (Table 2), which is in good agreement with reported reflection data of Ref [23]. A slight increase in reflection occurred at optical wavelengths from 650 to 1000 nm due to random distribution of the pores and increased roughness of PS surface [24]. Fig. 8 demonstrates an inverse correlation between porosity and optical reflection.

Fig. 8. Porosity percentage depending on reflectivity of PS.
The optical reflections decrease as the porosity increases due to the preferential formation of PS at the pore tips during etching process. The high porosity means an increase of the PS roughness; therefore the possibility of using the porous surface as an anti-reflection coating (ARC), is due to the surface texture which reduces the light reflection. The diffusion in PS is attributed to the roughness and related to the thickness of the porous layers [25]. The decrease in reflectivity is related to the optical diffusion and transmission at the porous and bulk interfaces [26,27].

The refractive index $n$ is a significant physical parameter in microscopic atomic interactions. Theoretically, the refractive index is related to the density and the local polarizability of these entities [28]. Many simple relationships between refractive index $n$ and the energy gap $E_g$ have been attempted [29–36]. Here, various relationships between $n$ and $E_g$ have been reviewed in order to validate the current work. As suggested by Ravindra et al. [29], the band gap and the high frequency refractive index, presented a linear relationship:

$$n = \alpha + \beta E_g,$$  \hspace{1cm} (4)

where $\alpha = 4.048$ and $\beta = -0.62 \text{ eV}^{-1}$. Inspired by simple physics of light refraction and dispersion, Herve and Vandamme [30] have proposed an empirical relation as:

$$n = \sqrt{1 + \left( \frac{A}{E_g + B} \right)^2}$$  \hspace{1cm} (5)

where $A = 13.6 \text{ eV}$ and $B = 3.4 \text{ eV}$. Ghosh et al. [31] had taken a different approach by considering the band structural and quantum-dielectric formulations of Penn [37] and Van Vechten [38]. Introducing, $A$ (contribution from the valence electrons) and $B$ (constant additive to the lowest band gap $E_g$), the expression was written as:

$$n^2 - 1 = \frac{A}{(E_g + B)^2},$$  \hspace{1cm} (6)

where $A = 25.5E_g + 212$, $B = 0.21E_g + 4.25$ and $(E_g + B)$ refers to an appropriate average energy gap of the material. Thus, we have tried these three models to determine the variation of $n$ with energy gap. In addition, the calculated values of the optical dielectric constant ($\varepsilon_\infty$) were obtained using the relation $\varepsilon_\infty = n^2$ [39]. The calculated refractive index and optical dielectric constant are given in Table 2. This is showing that the Ghosh et al. model is quite appropriate for solar cells studies and may be recommended for high efficiency calculation at high optical absorption and low spectrum reflection.

4. Conclusions

We successfully make porous silicon (PS) using electrochemical etching process of n-type silicon wafer. The SEM images taken at etching time of 120 min and illumination wavelength of 651 nm, exhibit high porosity percentage and uniform pores distribution. It is found that when a PS layer is fabricated with high porosity of 63.93%, the optical reflection is reduced. The use of low DC current density and long etching time results in PS with high porosity percentage and high photoluminescence response with blue shift and low reflectance. Our calculation suggest that Ghosh et al. model is quite appropriate for PS based solar cell studies and may be recommended for high efficiency calculation at high optical absorption and low spectrum reflection.

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