

Characterization of Nanostructure Silicon Layers' Act Antireflection

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ABSTRACT: Porous silicon (PSi) layers were fabricated on n-type crystalline silicon (Si) wafers of (100) orientations using photo-electrochemical etching (PECE) process at etching time of (1, 2, and 3 min), current density of 5 mA/cm², incident laser intensity of (5 mW) for blue laser (442 nm) and fixed electrolyte solution HF concentration (25%). Nanopores with an average diameter of 2.5 μm were formed in the n-PS (100) layer. These nanopores increased the porosity of the material to 52% for one- minute etching time compared with 55% porosity for 2-minute etching time and 65% for sample prepared at 3-minute. A greater red shift luminescence was observed in the sample prepared at 3-minute with those of the other samples. The lowest effective reflectance was obtained with one- minute etching time (PSi) layer that exhibited excellent light-trapping at wavelengths ranging from 450 to 750 nm. Solar cells were fabricated based on the (PSi) anti-reflection coating (ARC) layers. The current-voltage characteristics of the solar cells were examined under 100 mW/cm² illumination. A highly efficient (5.08%) solar cell was obtained with one- minute etching time layer compared with those solar cells with other layer types

KEYWORDS: Porous silicon, photo-electrochemical etching, solar cells, antireflection.

I. INTRODUCTION

Porous silicon (PSi), a nanostructured material, has attracted considerable attention as a measure to enhance the optical properties of silicon (Si). The formation of (PSi) layers on crystalline Si (Si) wafers using electrochemical etching (ECE) exhibits photo-luminescent and electroluminescent properties similar to those of semiconductors with direct energy gap [1]. (PSi) has emerged as an attractive material in the field of electronics and optoelectronics due to its broad band gap, wide optical transmission range (700–1000 nm), wide absorption spectrum, surface roughening, and good anti-reflection coating (ARC) [2]. The surface roughness and lower effective refractive index, which can reduce the reflection losses of sunlight radiation, are the primary factors that enhance (PSi) compared with Si [3]. In the visible (VIS) region, the refractive index decreases with increasing porosity, in contrast to the increasing edge absorption coefficient with an increase in porosity [4]. The porosity of the (PSi) layer increases with increasing current density and decreasing HF concentrations. This condition is also controlled by substrate doping [5]. Thus, a highly porous (PSi) layer can enhance the efficiency of solar cells by increasing light trapping into the active region [6]. This layer can also be used as ARC to serve as gutter centers and reduce the impurity levels of the Si substrate [7]. Moreover, a highly porous (PSi) layer further increases the efficiency and absorbs more light energy in Si solar cells [8]. A highly porous (PSi) layer is essential for high photoluminescence (PL) efficiency and in the acquisition of highly efficient solar cells. An inefficient luminescence results from an inhomogeneous material of low porosity [9]. The observed visible luminescence from the (PSi) layer is caused by the increasing energy band gap of the (PSi) layer compared with bulk Si [10].

In the present study, photo-electrochemical etching (PECE) processes were used to fabricate (PSi) layers on the n-type regions with (100) orientations using an etching time of (1, 2, and 3 min), current density of 5 mA/cm², fixed electrolyte solution HF concentration (25%). The morphologies and optical properties of the PS layers were also examined. The objective of the present study was to fabricate highly efficient solar cell using porous silicon (PSi) layer as ARC

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II. EXPERIMENTAL

N-type crystalline Si wafers (resistivity, $10 \Omega/\text{cm}$; thickness, $300 \mu\text{m}$; and orientation, (100)) were used as substrates. Before the etching process, the substrates were cleaned to remove the oxide layer using a solution of HF: H₂O (1:50) at 25°C to remove the native oxide and some ionic contaminants. (PSi) layers were fabricated by PECE process for n-type c-Si wafer with a 0.32 cm radius similar to the size of the opened-circular of the Teflon cell. Teflon was used to fabricate the ECE cell that had a circular aperture at the bottom that is sealed with Si samples. The cell was a two-electrode system connected to the Si samples as the anode and platinum (Pt) as the cathode. The cell was called PECE if the illumination was positioned over the n-type Si samples for maximum possible illumination and to generate the required holes for dissolution [5]. (Fig. 1).

The Si samples were placed in an electrolyte solution HF (48%):C₂H₅OH (98%) (1:1, by volume) to enable the conduction of electrons inside the solution. A current density of $5 \text{ mA}/\text{cm}^2$, incident laser intensity of (5 mW) for blue laser of wavelength (442 nm) and an etching time of (1, 2, and 3 min) were used to prepare the (PSi) layers on the front side of the Si samples. Synthesis was performed at room temperature (RT). The samples were rinsed in ethanol and dried in air after the etching process. The prepared samples of (PSi) layers with different porosities were used to fabricate solar cells .

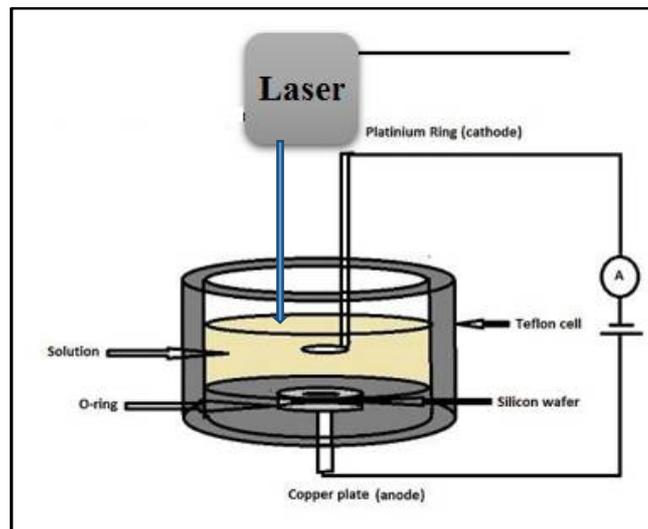


Figure 1. Schematic PECE cell set-up.

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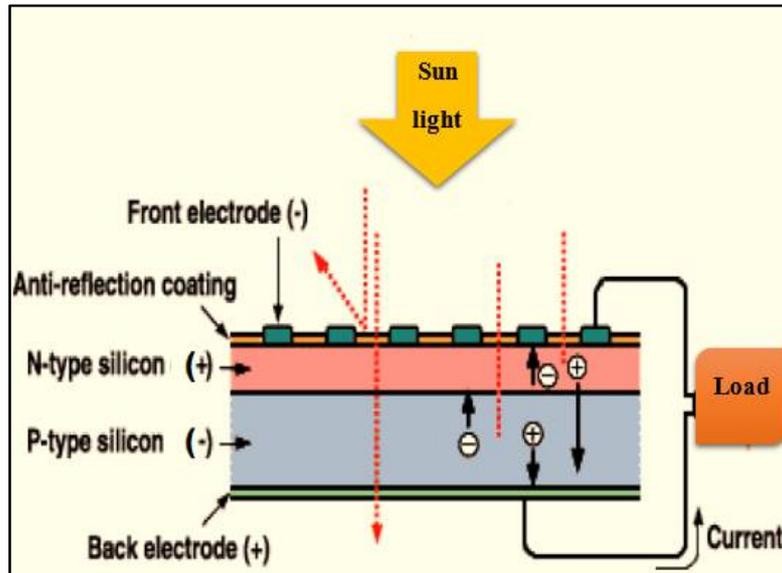


Figure 2 Schematic illustrations of solar cells with (PSi) layers formed on n-type Si (100)

When we use a cell with a p-type substrate, the p-n junction was also placed in the front side, and the solar cell was the front junction solar cell. Here, the front side will be the n-type, and the back side will be the p-type, as shown in Fig. 2. In addition, in the size of the fabricated solar cells was 1 cm² and the p-n junction was placed under the porous layer. To determine the surface morphology of the (PSi) layers we used scanning electron microscopy (SEM) type (Tescan VEGA 3 SB) made in USA with Atomic Force Microscope type (Angstrom Advanced Inc. AA3000) made in Boston (USA) and The structural properties of the porous silicon layer were characterized by XRD techniques. This measurement was carried out using a high resolution X-ray device (XRD 6000 shimadzu) supplied from (Japan). PL studies were performed for all (PSi) layers using UV/Visible Spectrophotometer (The Metertech SP-8001 UV/Visible Spectrophotometer), moreover the reflection properties of nano (Psi) were measured by using TF Prop Spectroscopic reflectometer (SR) series produced by Angstrom solar technologies (USA).

III. RESULT AND DISCUSSION

(PSi) layers were fabricated on the n-type Si wafers with (100) orientations at (1, 2 and 3 min) etching time with fixed HF concentration and current density. Fig. 3(a) shows an SEM image of the (PSi) layer formed at one-minute etching time by using blue laser (442 nm), The Star fall – shape (special and dramatic structure) could be seen in figure (3 -a), It is the dominant form in the distributions of pores on the sample surface with high homogeneity, the pores had bigger diameter and higher density compared with pores produced 2 minute etching time as shown in figure (3 - b). the pores shape in the (PSi) layer in figure (3 - b) has the Starfall – shape, pillar shape and cylindrical shape with different distributions (inhomogeneous distribution), Additionally, highly dense pores were evident.

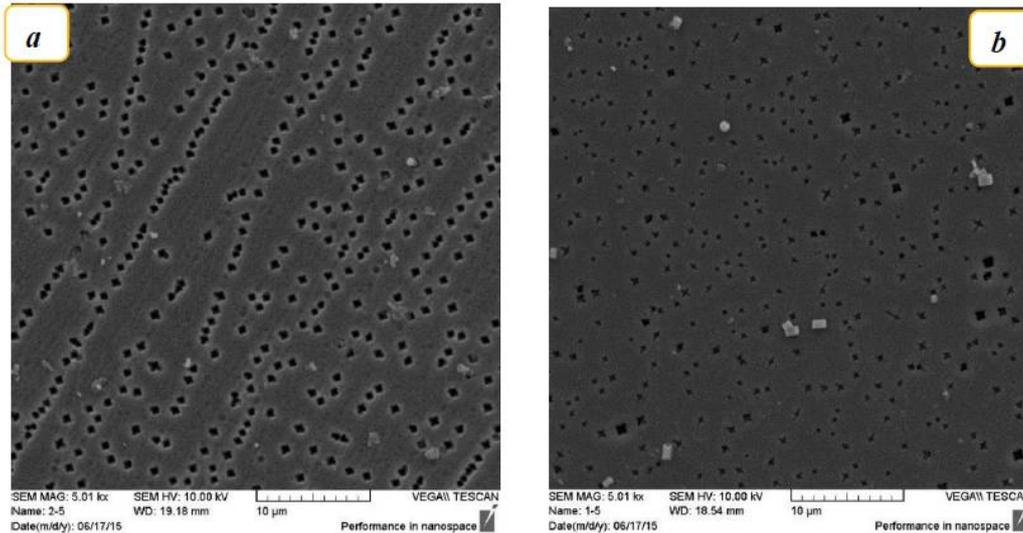


Figure 3.: SEM images (top-view) of PSi layer prepared at (blue 442 nm) with Etching time of (a) 1 min (b) 2 min

This variation in pore width might be due to the non-uniform of the charge carrier's distribution of illumination, consequently leads to non-uniform hole-photo-generation, resulting in different pore widths. The non-uniform of the charge carrier's distribution of illumination is attributed to the fact that charges take the easier path to get the surface with the direction of electric field and avoid resistance of material. The average pore diameter (d) for the (PSi) layer formed on silicon surface was $2.5 \mu\text{m}$ for one-minute etching time, while the diameter decrease to $0.5 \mu\text{m}$ when the etching time increase to two- minute, the diameter calculated using (image J program). From the Atomic Force Microscope (AFM), we were able to get the results of the distributions as well as the reluctance of the pore surface of the porous silicon layer as shown in the figure (4.8) for samples prepared by blue laser wavelength (442 nm) with different etching times (1 and 2 min).

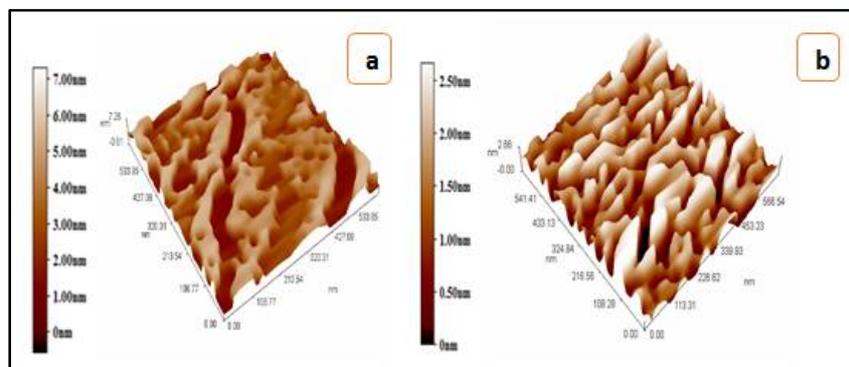


Figure 4: AFM images of PSi layer prepared at (blue 442 nm) with Etching time of (a) 1 min (b) 2 min

We observed for (AFM) images for the samples the average roughness was of (1.14 nm) and root mean square of (1.32 nm) for layer prepared at (1 min), while the average roughness (S_a) and the root mean square (S_q) for a layer processed at (2 min) etching time was (0.66 nm), (0.761 nm) respectively. The results of X- ray diffraction analysis give us a clear picture of the structural properties for (PSi), from the results one can calculate the silicon nano-sizes inside the pore-like structure in addition to determine the nature of the porous layer (crystalline or amorphous) [74]. The silicon nano-sizes were calculated by using **Sherer's** formula and the structural properties were analyzed based on the X-ray

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diffraction measurement of porous silicon samples. Figure 5 (a & b), represent the X-ray diffraction pattern of porous silicon.

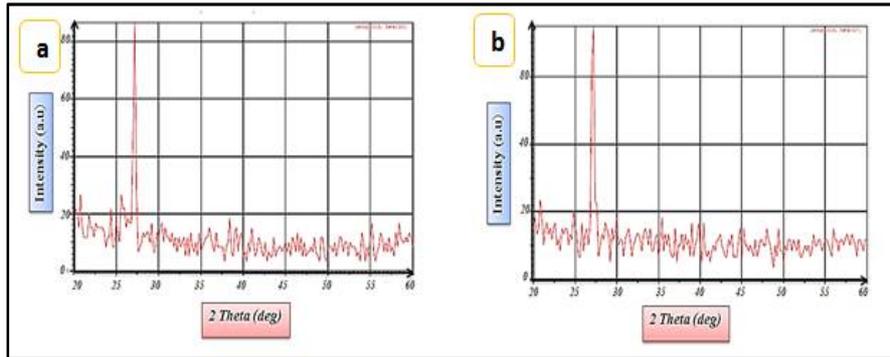


Figure (5) represent the X-ray diffraction pattern of porous silicon prepared at
(a) 1 min etching time (b) 2 min etching time

show the X-ray characteristics of porous silicon samples fabricated at the same preparation condition but with blue illumination. This pattern shows the appearance of the same peak and with slight different in the peak position at (27.174) 2θ angle with intensity of 34 (a.u) for 1-minute etching time. Furthermore, for 2-minute etching time the value of the single peak at (24.418) 2θ angle with intensity of 5 (a.u).

Table (4.5): Shows the silicon nano-size, etching time, energy gap, intensity and FWHM of PSi prepared under blue wavelength at current density 5 mA/cm².

| Wavelength (nm) | Etching time | θ/2 | Peak height (a.u) | FWHM (β) | Grain Size L (nm) | Energy gap of PSi (E _g) |
|-----------------|--------------|----------|-------------------|----------|-------------------|-------------------------------------|
| BLUE 442 nm | 1 | 0.237021 | 34 | 0.004239 | 31.97 | 1.89 |
| | 2 | 0.212986 | 5 | 0.002909 | 46.60 | 1.58 |

The porosity of was calculated using Eq. (1) [14],

$$P(\%) = \frac{(m_1 - m_2)}{(m_1 - m_3)} \dots\dots\dots (1)$$

where m₁ is the sample weight before anodization, m₂ is the sample weight after anodization, and m₃ is the sample weight after removing the PS layer with 3% KOH solution for 5 min [6]. The porosity has a lower value of about 45% at shorter etching time (1 min). The increase in the time of the etching process to (3 min) led to increase the porosity to a higher value of about (65%).

$$E_g^* = E_g + \frac{88.34}{L(1.37)}$$

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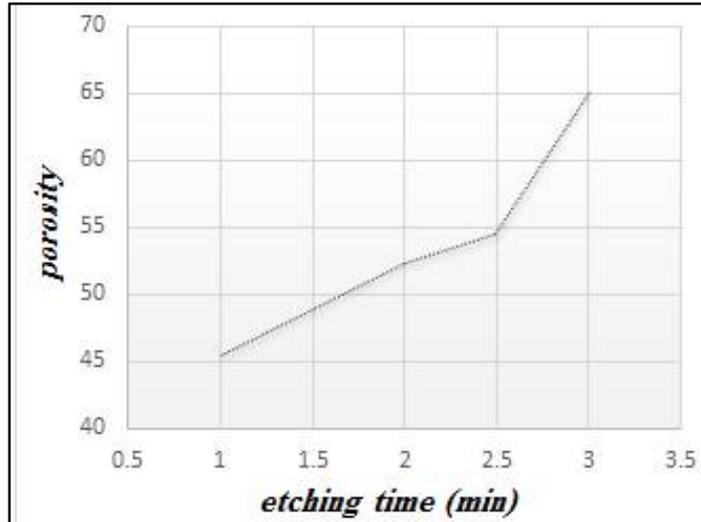


Figure 5: Variation of the porosity with etching time of (PSi) by used laser wavelength 442 nm (Blue illumination).

Form the PL peak we can calculate the energy band gap of the (PSi) layer by using equation (2)

$$E_g^* = E_g + \frac{88.34}{L(1.37)} \dots\dots\dots (2)$$

where E_g^* is the energy band gap of the (PSi) layer, E_g is the energy band gap of bulk Si. Table (1) show the results of PL measurement.

Table (1): Illustrates the energy gap, silicon nano-crystallites size of (PSi) prepared at different etching time (BLUE illumination)

| Etching laser illumination (nm) | Etching time (min) | PL peak position (nm) | PL Peak intensity (a.u) | Energy gap of PSi (eV) | Average PSinocrystallites (nm) | FWHM |
|---------------------------------|--------------------|-----------------------|-------------------------|------------------------|--------------------------------|------|
| UV 365 | 1 | 611 | 1781 | 2.029 | 68.41 | 27 |
| | 2 | 615 | 4202 | 2.016 | 66.07 | 29 |
| | 3 | 609 | 1942 | 2.036 | 69.67 | 30 |

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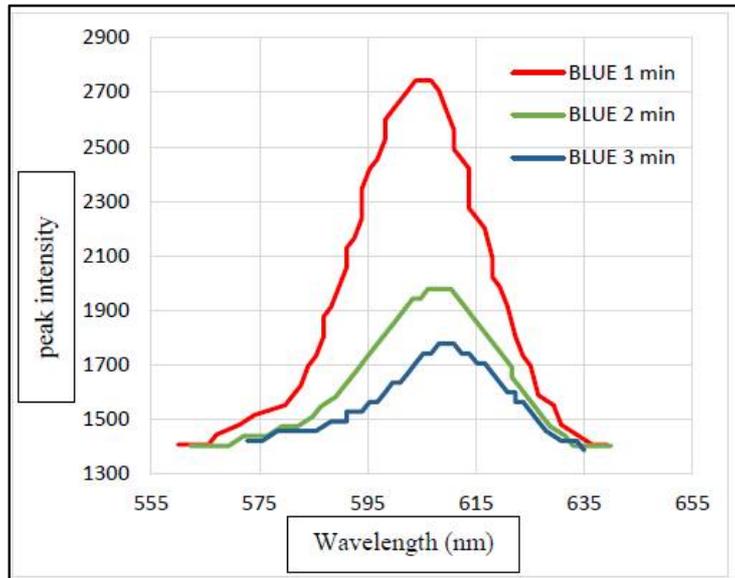


Figure (4.33): Shows the PL characteristics of (PSi) prepared with 5 mW/cm² illumination intensity of blue 442 nm laser wavelength at (1, 2 & 3) minute etching time

This figure showed that the photoluminescence characteristics have sharp peak intensity at different wavelengths which refer to the fact that the porous layer has specific nano-sized silicon distribution. Since the photons energy is greater than the energy gap of the generated nano-crystallites, therefore, the efficient absorption could be occurred leading to generate a wide range of silicon nano- sizes within the (PSi) layer.

The changing in porous reflectivity is generally due to the nature of porous layer, where this layer has light scattering regions and also because the large value of the surface area to volume ratio of about (500 m²/cm³), which improve the optical absorption inside the porous layer and hence reaching a low reflectivity.

Figure (6 - a) represents the reflectivity of reference sample (mirror- like) silicon surface as a function of wavelengths, the reflectivity has a maximum value of about 50% at wavelength of (400 nm) and its value decreases with reached at wavelength of (850 nm). This large value of reflectivity of silicon solar cell in the spectral range (400 nm - 850nm) refers to high refractive index at air- Si interface The maximum value of reflectivity at (850 nm), is vary from (17.5 %) at (1 minute) etching time to (20.5 %) at (2 minute) etching time and (19 %) for (3 minute) etching time, where the surface reflectivity of porous sample at short wavelength regime vary from (10 %) at (1 minute) etching time to (17.5 %) at (2 minute) etching time and (17.8 %) for (3 minute) etching time at (500 nm).

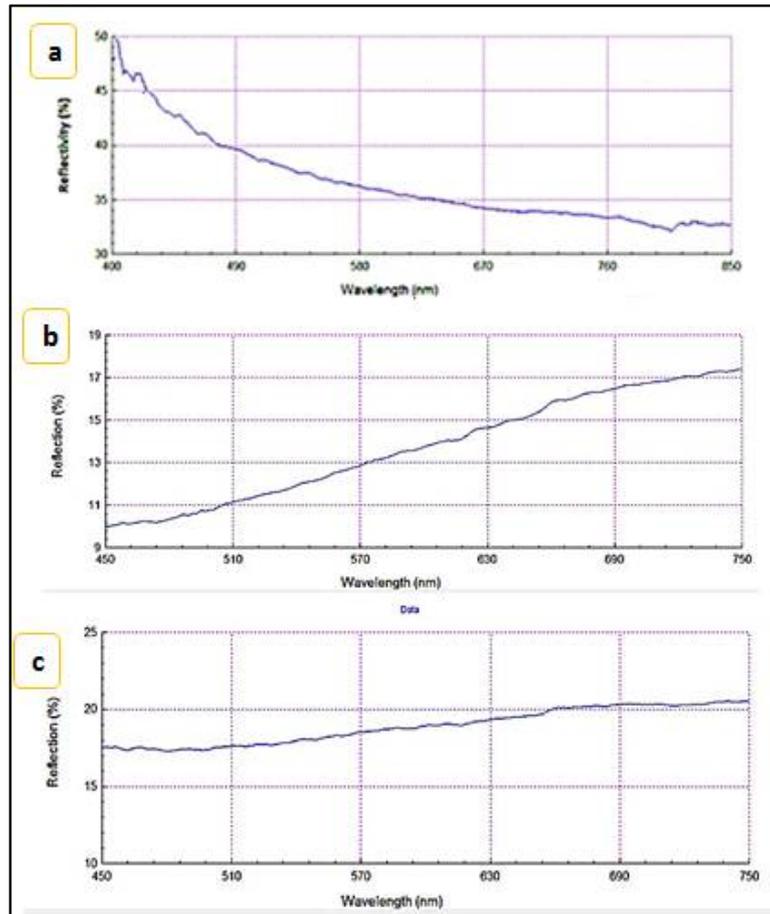


Figure (4.25): The reflectivity of (a) reference sample (mirror- like) silicon surface (b) porous silicon prepared by (LAE) with blue (442 nm) wavelength and etching time (1 min). (c) porous silicon prepared by (LAE) with blue (442 nm) wavelength and etching time (2 min).

The relatively high reflectivity of a silicon solar cell without an antireflection layer is due to the large refractive index discontinuity existing at the air–silicon interface. By placing a layer (PSi) of intermediate refractive index onto the silicon surface, this large index discontinuity is broken into two smaller steps leading to a lower reflectivity.

IV. CONCLUSIONS

This work regarded as a main contribution to the field of characterization and preparation of porous silicon and its applications in the field of antireflection coating (ARC).

- I. Our conclusions could outline as follows:
- II. Current density with Laser-Assisted Etching (LAE) process and short wavelengths illumination could be considered as a very useful technique to synthesis porous silicon appropriate for ARC for solar cell applications.
- III. The porous layer thickness of (PSi) produced with UV illumination was lower than that for Blue illumination.
- IV. The surface morphology for the porous silicon indicated two different structures that were circler pore-like structure at UV illumination wavelength and cross pore-like structure at long illumination wavelength.
- V. The pore width of (PSi) produced by UV wavelength was smaller than that of blue illumination with respect to etching time.

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VI. The reflectivity measurements of (PSi) layer were much lower than that for bulk silicon (Si).

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