Structural, Morphological and Optical properties of n-type Porous Silicon-effect of Etching Current Density

H K Abood¹ and F A-H Mutlak¹*
¹University of Baghdad, College of Science, Physics Department, Baghdad, Iraq

*Corresponding author's e-mail: Falah.mutlak5@gmail.com

Abstract. Porous silicon layers have been prepared from n-type silicon wafers of (111) orientation. XRD, AFM, reflectivity and PL have been used to characterize the structural, morphological, and optical properties of porous silicon. The influence of varying etching current density in the anodizing solution, on structural and optical properties of porous silicon has been investigated. It is observed that pore size increases with etching current density and attain maximum for 56 mA/cm² and then decreases. The PL spectrum peak shifts had been slight towards the higher energy side, which supports the quantum confinement effect in porous silicon. The reflectivity shows that the porous silicon surface lower reflectance which is due to the very thin layer of porous silicon and changed refractive index profile at the interface of the bulk silicon and porous silicon material.

Keywords: Porous silicon; Si microstructures; Etching; Solar cell.

1. Introduction
Silicon thin films are used in many devices in various fields of applications such as optics, optoelectronics and microelectronics [1]. A band gap of silicon 1.12 eV leads to efficient detection of visible light and conversion of sunlight into electricity. There is a wide range of interest in improving the responsivity of silicon detectors in the visible and the near-infrared (near-IR) regions of the electromagnetic spectrum [2]. In order to increase the efficiency of actual solar cells, many different ways are currently being developed by researchers. Through the focus of work on the nano and microstructurization of the surface [3]. Nanostructured solar cells offer several advantages for solar cells including; (1) the ability to exceed a single junction solar cell efficiency by implementing new concepts; (2) the ability to overcome practical limitations in existing devices, such as tailoring the material properties of existing materials or using nanostructures to overcome constraints related to lattice matching and; (3) the potential for low cost solar cell structures using self-assembled nanostructures [4]. PS was discovered by Uhlir in 1956 [5], and in 1990, Canham [6] showed that certain PS materials can have large photoluminescence (PL) efficiency at room temperature in the visible region. This result was surprising, since the PL efficiency of bulk silicon is very low, due to its indirect energy band gap and short non-radiative lifetime. The reason for PS giving surprising result was the partial dissolution of silicon, which causes i) the formation of small silicon nanocrystals in the PS material: ii) the reduction of the effective refractive index of PS with respect to bulk silicon, which
increased the light extraction efficiency from PS: and iii) the spatial confinement of the excited carriers in small silicon regions where non-radiative recombination centers are mostly absent. In general, it can be said that the PS is an interconnected network of air holes (pores) in Si. Porous structures are formed with the mechanism proposed by Lehmann and Gosele [7]. There are three different kinds of etching techniques for monocrystalline silicon solar cells: photochemical-etching, electrochemical-etching and photo electro chemical etching [8]. The beneficial effect of the micro texturized Si obtained by femtosecond laser was demonstrated by Kolasinski et al. [9, 10] which showed Laser assisted etching in aqueous fluoride solutions allows for selected area formation of nan crystalline porous silicon. Mutlak. [11] Prepared a laser-micro textured Si structure which reduces the reflection of a Si surface. Laser surface texturing method was achieved on Si solar cell by UV femtosecond laser. Drevinskas et al. [12] demonstrate that selective KOH etching reveals high contrast nan gratings without affecting the unmodified silica lattice and leads to the control of optical dispersion and enhancement of the retardance exhibited by the nanostructures. Mutlak et al. [13] deposited the SnO$_2$ NPs on chemically etched n-type silicon substrate. The reduction in SnO$_2$ NPs size accompanied by increasing the surface area to volume ratio and photoreaction of these nanoparticles led to increases of the responsivity, quantum efficiency and detectivity of this UV region detector.

In this paper, we improve the method used to enhance the absorption efficiency of the silicon solar cells by using photo electrochemically anodized, and the formation of nanostructure porous silicon layers is observed and its feature characteristics are studied.

2. Experimental

2.1 Chemicals

Silicon wafer of n-type (111) with a resistivity of 0.015 Ω.cm and thickness 508 μm was used the following solvents were used as media deionized water, organic ethanol (ScharlauCo., CH$_3$CH$_2$OH, 99.9% purity) and HF (48%, SOLVOCHEM, UK).

2.2 Preparation of PS

The Si wafer cut off into (2×2 cm$^2$) pieces, rinsed with ethanol to clean the surface from any contamination after that rinsed with 5% Hydrofluoric acid (HF) to remove the native oxide and dried in presence of nitrogen. A thin Aluminum film was deposited on back side of Si wafer to create ohmic contact.

The experimental set – up of laser-assisted etching for produced PS samples is presented in Figure 1. Etching cell was made from Teflon with bottom part from stainless steel disk which was placed for contact purposes. Then the silicon wafer was placed and a rubber O-ring was used before placing the upper part which has a center circular of 1cm$^2$ to allow the electrolyte solution touch the silicon wafer. Two electrodes were used to apply current across the cell, the first one was was the stainless steel disk below silicon wafer and the other was made of gold mesh immersed in the HF solution. The electrical

![Figure 1. Experimental set-up of photo-electrochemical anodization process.](image-url)
circuit was completed by QJEDC regulated power supply (QJ3005XIII), and and diode laser of wavelength 532 nm and power of 200 mW was used to illuminate the Si surface. Laser power was obtained after calibration by using (Genetic- EO SOLO2) power meter. The Beam expander was utilized for expand the laser beam to lighting all etching Si area. The PECE process was carried out with different current density (06, 16, 26, 36, 46 and 56 mA/cm$^2$) and constant HF concentration (15%) for 10 minutes. After etching process, the PS sample was rinsed by pentane, ethanol and dried with stream of air.

2.3 Measurements
The surface morphology and roughness of prepared samples was obtained by atomic force microscopy gave a direct surface image of porous silicon layer. A CSPM-AA3000. AFM instrument was used. The photoluminescence was measured by using a PerkinElmer LS-45 Fluorescence spectrometer. Structural properties of PS have been investigated by X-ray diffraction techniques. A SHIMADZU (XRD-6000, 220/50Hz, JAPAN) of 1.54 Å from Cu-K$\alpha$ was used. The optical properties of the porous silicon were studied by optical reflectance spectroscopy. The spectra were obtained at room temperature. UV-VIS, Perkin Elmer Lambda 950 spectrophotometer was employed to study the optical Reflectance (R) for PS/Si layer prepared in different conditions for wavelength interval between 400-800 nm.

3. Results and discussion
XRD was used to investigate the size of the crystallites of the PS and to estimate the crystalline degree of etched samples. XRD pattern of bulk silicon become a very sharp peak at 2$\theta$ = 28.8° showing the single crystalline nature of the wafer. This peak becomes very broad with varying full-width at half maximum (FWHM) for different anodization current densities as shown in Figure 2. Consequently, we can confirm that the PS layer remains crystalline, but it is slightly shifted to a smaller diffraction angle.

The crystallites size obtained for PS samples are shown in Table 1, when estimated by the Scherrer's equation, a significant crystallites size decrease trend can be clearly noted on urrincreasing current density.

Figure 3 shows the 3D AFM image and diameter values distribution of PS samples prepared under different current density of porous silicon in which the irregular and randomly distributed nanocrystalline silicon pillars and voids over the entire surface can be seen. However, increasing in current density orders the small pores to exhibit cylindrical shapes giving rise to larger pore diameter. The morphology characteristics of PS samples are presented in Table 2. The average pore diameter appears in good agreement with classification of mesoporous. At low current density, small pores are formed surrounding by thick columnar structure network of silicon walls. When the current density is increased the pore with large diameter and thin columnar walls is formed.

Figure 4 shows the room temperature PL spectra of various samples. The energy band gap (Eg) values were estimated to be 1.768, 1.771, 1.773, 1.773, 1.776 and 1.779 eV for current densities of 6 mA/cm$^2$, 16 mA/cm$^2$, 26 mA/cm$^2$, 36 mA/cm$^2$, 46 mA/cm$^2$ and 56 mA/cm$^2$, respectively. The observed blue shift in the PL peak with increasing anodization current density was attributed to quantum confinement effect, which led to an increase in the energy band gap. The FWHM values for different peaks with increasing current density displayed slight narrowing. The decrease in PL intensity with the increase of anodization current density was attributed to the enhanced recombination probability of the carriers that are strongly confined within the nanostructure, where the nature of the band gap is transformed from indirect one to quasi-direct one. The PL peak shift, narrowing of FWHM, and an increase in the peak intensity at 56 mA/cm$^2$ are consistent with previous findings [14, 15].

It can be seen that the reflectivity of PS is raised with increasing the current density from (6 to 56 mA/cm$^2$) as shown in Figure 5. Hence, at low current density etching (6 and 16 mA/cm$^2$), the porosity
of porous silicon layer increased, and refractive index will reduce. Thus the reflectivity of porous silicon is reduced. Reduced reflectivity is also attributed to the light scattering and increased light trapping at wavelength (400-800 nm). The scattering light may be due to the surface roughness at the

![Figure 2. X-ray diffraction patterns for PS layers with different etching current density.](image)

| T \(_{x}\) (°C) | x  | a (Å) | b (Å) | c (Å) | V (Å) \(^2\) | c/a (Å) | \(\rho_m \) (gm/cm\(^3\)) | V2223% | V2212% |
|---------------|----|-------|-------|-------|--------------|---------|-----------------|---------|---------|
| 820           | 0  | 5.403 | 5.477 | 37.007| 1095         | 6.849   | 1.428           | 69.632  | 29.478  |
|               | 0.2| 5.406 | 5.322 | 36.671| 1055         | 6.783   | 1.507           | 41.543  | 57.567  |
|               | 0.4| 5.403 | 5.352 | 36.846| 1065         | 6.819   | 1.503           | 68.854  | 30.256  |
| 830           | 0  | 5.365 | 5.454 | 37.212| 1088         | 6.936   | 1.436           | 79.554  | 19.556  |
|               | 0.2| 5.447 | 5.361 | 37.149| 1084         | 6.820   | 1.452           | 51.723  | 47.387  |
|               | 0.4| 5.454 | 5.465 | 37.267| 1110         | 6.832   | 1.456           | 68.934  | 30.176  |
PS-Si interface, whereas roughness is attributed to the etching parameters affect the surface characterization. The high degree of roughness of the PS surface implies the possibility of using the porous layer as an antireflection coating for solar cells because the surface reduces the light reflection. Our results are in consistent with previous studies [16, 17].
Figure 3 Cross-sectional view of AFM images of the PS obtained at different anodization current density of: (A) 06 mA/cm$^2$, (B) 16 mA/cm$^2$, (C) 26 mA/cm$^2$, (D) 36 mA/cm$^2$, (E) 46 mA/cm$^2$ and (F) 56 mA/cm$^2$.

Table 2 The analysis of the PS morphology characteristics prepared at different current densities.

| J (mA/cm$^2$) | Average diameter (nm) | Average roughness (nm) | Root mean square (nm) |
|---------------|------------------------|------------------------|-----------------------|
| 06            | 24.30                  | 14.9                   | 17.1                  |
| 16            | 24.79                  | 5.14                   | 5.95                  |
| 26            | 34.16                  | 2.71                   | 3.13                  |
| 36            | 35.96                  | 1.88                   | 2.17                  |
| 46            | 47.86                  | 3.01                   | 3.14                  |
| 56            | 55.51                  | 6.35                   | 7.33                  |

Figure 4 Room temperature PL spectra of PS samples different anodization current density.
4. Conclusions
In this paper, we have prepared micro textured Si structure, which reduces the reflection of a Si surface. Laser-assisted etching method was accomplished on Silicon by laser. The effects of anodization current densities on the morphology and PL spectra of as synthesized PSi were analyzed. It was demonstrated that by varying the anodization current density it is possible to control the porosity and the visible light emitting properties of such PSi. Good quality PSi samples were achieved. PL spectra revealed prominent peaks together with large blue shift, which supported the presence of strong nanoporous structures. Strong surface roughness is established to be responsible for the reduction of the Si crystallite size at higher anodization current density. As a result this approach leads to enhance Si cell efficiency. The current method is much cheaper and simpler than the reactive – ion etching (RIE).

References

[1] Hermann J, Benfarah M, Bruneau S, Axente E, Coustillier G, Itina T, Guillemoles J, and Alloncle P 2006 J. Phys. D: Appl. Phys. 39 453.
[2] Maurizio C, Giuseppe C, Mario I, Ivo R and Luigi S 2010 Sensors 10 10571.
[3] Pedraza A, Fowlkes J, Lowndes L 1999 Appl. Phys. Lett. 74 2322.
[4] Honsberg C, Barnett A, Kirkpatrick D, 2006 4th World Conference on Photovoltaic Energy Conversion, Hawaii, USA, 7-12 May, Record of the IEEE 2 2560.
[5] Uhlir A 1956 Bell Syst. Tech. J 35 333.
[6] Canham L 1990 Appl. Phys. Lett. 57 1046.
[7] Bisi O, Stefano O and Pavesi L 2000 Surface Science Reports 38 1.
[8] Wang X, Tebib A, Veschetti Y and Bastide S 2011 Phys. Status Solidi A 208 215.
[9] Kolasinska K, David M and Mona N 2006 J. Vac. Sci. Technol. A 24 1474.
[10] Gattass R and Mazur E 2008 Nat. Photonics 2 219.
[11] Mutlak F A-H 2014 Turk J Phys 38 130.
[12] Drevinskas R, Mindaugas G, Beresna M, Bellouard Y and Kazansky P 2015 Optics Express 23 1428.
[13] Mutlak F A-H, Taha A B and Nayef UM 2018 Silicon 10 967.
[14] Behzad K, Yunus W, Talib Z, Zakaria A and Bahrami A 2012 International Journal of Electrochemical Science 7 8266.
[15] Al-Douri Abd H Y, Ahmed N and Hashim M 2013 International Journal of Electrochemical Science 8 11461.
[16] Ramizy A, Hassan K, Omar Y Al-Dourib, Mahdi M A 2011 Applied Surface Science 257 6112.
[17] Salman K, Hassan A Z, Omar K 2012 Int.J.Electrochem.Sci. 7 376.