Porous Silicon Refractive Index Measurements with the Assistance of Two types of Lasers

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Abstract

Porous Silicon (PSi) samples with (100) orientation n-type were prepared by photo-electrochemical etching process for different variable parameters and fixed electrolyte solution $HF:C_2H_5OH:H_2O$ (2:3:3). Physical and optical properties of PSi would be varied with the variation of process parameters such as current density, anodization time and laser wavelengths. Two types of 50 mW diode lasers were chosen, 473 nm Blue & 532 nm green at 20 mA/cm^2 & 15 min etching time to assist the iodization process. The band gap of the fabricated layer has raised up to (2.9 eV) which is more than twice its original value for the c-Si (1.12 eV).

Exploiting the obtained gap energy values, the refractive index of porous silicon layer was calculated depending upon Vandamme empirical relation. It was observed that the porosity is modifiable through etching conditions, which in turn makes refractive index also modifiable. Thus, the calculation depended on taking certain parameters as the current density and etching time in order to compare the effect of applying the two laser wavelengths. AFM was applied to observe the homogeneity and roughness of the PSi mono-layer. The results are in a very good agreement with the range of the refractive indices of PSi and the illumination with green laser gives a better conclusion to use in solar cells as a good absorber and a bad reflector.

Keywords: Porous silicon, porosity, refractive index, etching, current density, AFM.

Introduction

Porous silicon (PSi) attracts much interest as promising silicon based optoelectronic material for its efficient visible room temperature photoluminescence [1]. The attribution for that is the quantum confinement of the charge carriers in Si nanocrystals and its modifiable refractive index [2]. The other application of interest is the improving of the efficiency of solar cells [3]. This leads to consider the formation of PSi layer as an enhancement to optical properties of the pure silicon (Si). It shows different features in comparison to the bulk silicon such as shifting of fundamental absorption edge into the short wavelength [2,3].

Varying the affected parameters as the supplied current results to porosity variation and consequently, refractive index tunability is possible. Due to the tunable refractive index property of PSi, it can be fabricated into mono or multilayered structures such as anti-reflection coatings (ARC) [4]. The objective of this study is to determine the main optical characteristics of the PSi-monolayer: i.e., (refractive index) depending on porosity and thickness which go along with changing in gap energy. These characteristics have been previously calculated with several methods and the comparison between some of these results and the results that depend on the gap-energy obtained in this work is presented.

There are several parameters that affect the formation (anodization) **process** as: etching time, current density, HF concentration, crystallo-graphic orientation, temperature, Illumination during the etch, essential for n-type substrates, the type of the wafer doping and resistivity, ambient humidity, PH of the solution.

The most commonly used parameter for the formation of porous silicon is the current density in the DC-regime. Under the appropriate current density and chemical solution formulation, the silicon fine holes were produced. However, for any current to pass the Si/electrolyte interface, it must first change from electronic to ionic current [3]. Increasing current density would results in increasing in porosity and consequently increasing the band gap value attributed to change in the Si structure size [3,5]. Etching time has a similar importance as the current density; this parameter is responsible of controlling the PSi layer thickness. Increasing anodization time would result in an increase in layer thickness. However, as the thickness increases, the exposure of the PSi to the electrolyte will be longer, thus, the porosity increases due to the extra degeneracy of the layer in HF solution. The porous layer thickness depends on the etching time, due to the fact that the number of photons irradiated on the sample increased with time [6].

On the other hand, some n-type etch configurations require illumination of different types. The purpose of the illumination is to excite electrons in the silicon to the conduction band, creating electron-hole pairs [7]. The holes participate in the etching process, so the illumination helps to provide some control over the etch rate. Diode lasers were chosen and applied to enhance the anodization process, i.e., 473 nm Blue & 532 nm green at 20 min etching time. These are to be optimized which one is the best enhance PSi refractive index.

Index of Refraction related with Pores

Different models have been investigated to calculate the refractive index of ARCs for the reduction of reflectance of silicon solar cells. Some models depend in their calculation upon reflectance from the PSi as a thin film [7], others depends on photon scattering [3] or on the local electric field [9]. Most of these models concluded that the refractive indices of PSi are ranging from 1.2 up to 1.9.

Vandamme proposed the empirical relation as[5,9,10]:

$$n = \sqrt{1 + \frac{A}{B + E_{gpSi}}} \quad \text{.................} \ (1)$$

where A = 13.6 eV and B = 3.4 eV.

The diameter (d) of the pores of PSi can be calculated relying on PSi- gap energy E_{gpSi} equation that concluded from the peaks at PL graphs, i.e., :

$$E_{gpSi} = \frac{h^2}{8d^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] + E_{gSi} \text{........}(2)$$

here E_{gSi} is the energy of c-Si gap, h is the Planck's constant (4.13×10-15 eV·s),m_e^* and $m_h^*$are the electron and hole effective masses, respectively. Its been shown that at 300 K, (m_e^* = 0.19 m_o, m_h^* = 0.16 m_o, and m_o=9.109x10^{-31} kg) [5,6].

Equation (1) would be applied in this work to estimate the refractive index of PSi depending on the E_{gpSi}values concluded from the PL graphs of the PSi samples tested.

Experimental Details

1. Preparation of PSi samples was done by photo-electrochemical etching of silicon in HF-based solutions at room temperature doped n-type(100) oriented Si wafer(ρ=0-100Ωcm) in a solution of concentrations 48% HF, 99.90% ethanol and deionized water (HF:C_2H_5OH: H_2O) at a volumetric ratio of 2:3:3 respectively.

Firstly,the samples were sliced into pieces of (1×1.5 cm) ,i.e., of area (1.5 cm^2) shown in Figure (1) which is suitable for the area of the 0-ring in the Teflon cell (0.5 cm diameter). Thus the anodized area would be 0.1963 cm^2 which was illuminated by the laser light simultaneously. Secondly, the samples were rinsed with ethanol to remove any dirt hence immersed in diluted (10%) Hydrofluoric acid (HF) for 10 min to remove any native oxide layer. This is followed by rinsing with ethanol again and left for a few minutes in the ambient atmosphere to dry, thus maintaining these samples immersed and stored in a plastic containers filled with methanol to prevent the formation of oxide layer once again at their surfaces

Figure (1): Sliced samples.

2. Every sample then placed in the bottom of a Teflon singlet anodizing system and fixed by stst sheet as a support material which are considered as the Anode. A platinum mesh rod, was placed perpendicular to the Si surface at a distance of 1 cm considered as the cathode. The resulting samples were obtained by varying the current density at a constant etching time or vice versa.
3. To approach the beneficial solution mixture, several experimental trials were done to explore the most suitable ratio for the purpose of this work.
4. The anodization cell layout is shown in Figures (2), (3) and (4),

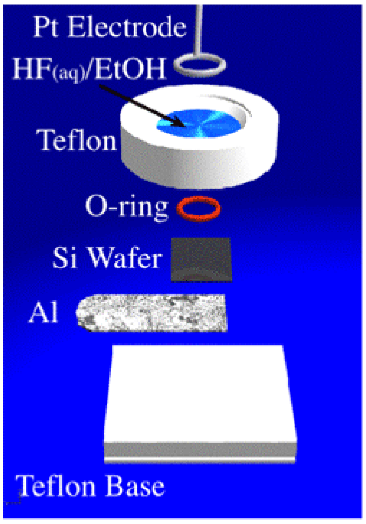

Figure (2): Fundamental cell layout

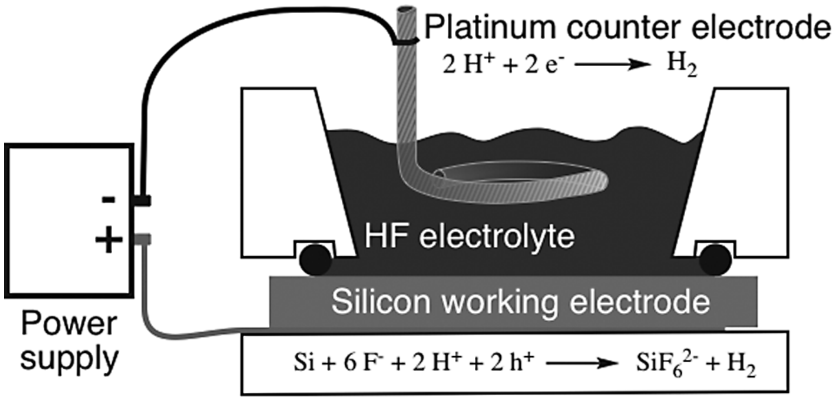

Figure (3): Anodization circuit layout.

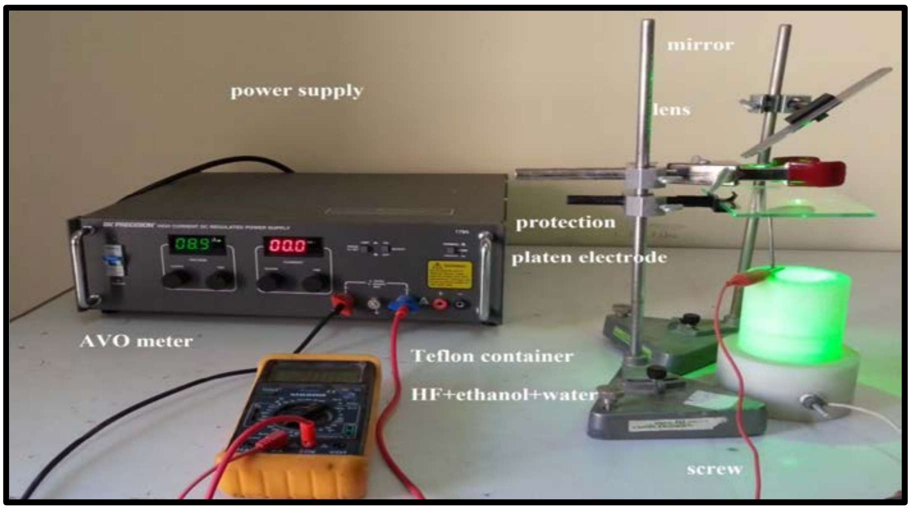

Figure (4): Photographic image of PECE system.

1. This technique has been adapted in this work with the assistance of green laser (532 nm) as well as a laser wavelength that did not applied before up to our knowledge, i.e., blue laser (473 nm).
2. Other optical accessories were used, i.e., a mirror was mounted over the Teflon cell to reflect the laser beam with an angle of 45^0normally upon the n-region of the Si-sample. A lens of focal length (10 cm) was used as well to spread out the laser light on the whole silicon illuminated area (0.25 cm^2).
3. For 50 mW laser power: the samples were prepared under, (10, 15, 20, and 25) mA/cm^2 current densities under a fixed etching time of 15 min; and an etching time of (10, 15, 20, and 25) min at a constant current density of 20 mA/cm^2. This is repeated for both available laser wavelengths (blue & green) selecting the 20 $mA/cm^2$for comparison.
4. Photoluminescence (PL) Microscope has been applied to test the photoluminescence spectrum of the p-n junction porous silicon samples at room temperature using He-Cd laser (325nm).
5. Also, AFM test was applied to ensure the homogeneity of the PSI surfaces and its roughness as well.

Results and Discussion

For the purpose of this paper, the concentration is on the results of Photo-luminescence (PL) Measurements and Plots in order to obtain the gap energy for every PSi sample using a different applied laser wavelength. The E_{gPSI} is then be employed to calculate the refractive index applying eq. (1). These results are obeyed to compare with other refractive index calculation methods. The following plots represent the investigations and tests achieved by the PL device for the different samples formed depending on eq.(2).

Figures (4) and (5) show the PL spectrum of the PSi prepared with the assistance of two types of lasers : blue (473 nm) and green (532 nm) of (50 mW each).

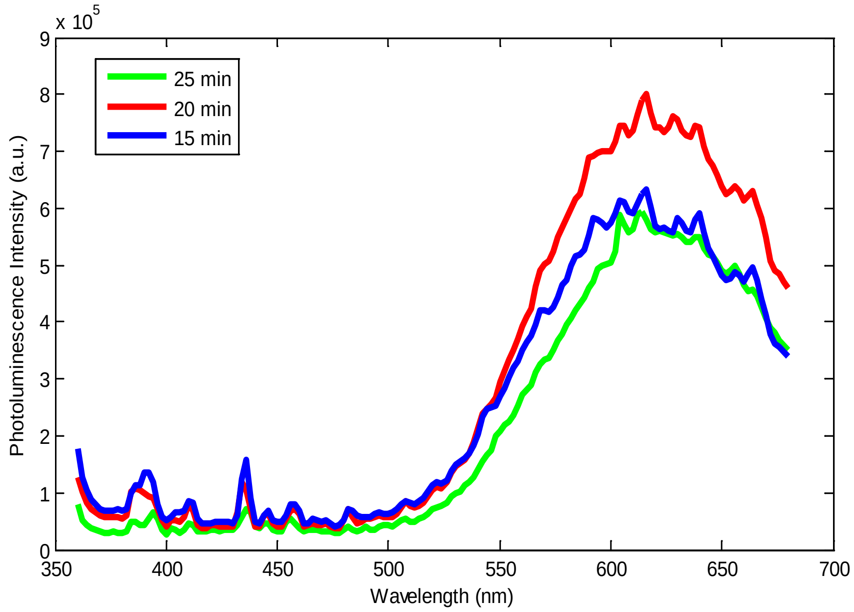

Figure (5): Photoluminescence spectrum of the PSi sample prepared with the assistance of blue laser (50mW) at different etching times (15,20,25) min.

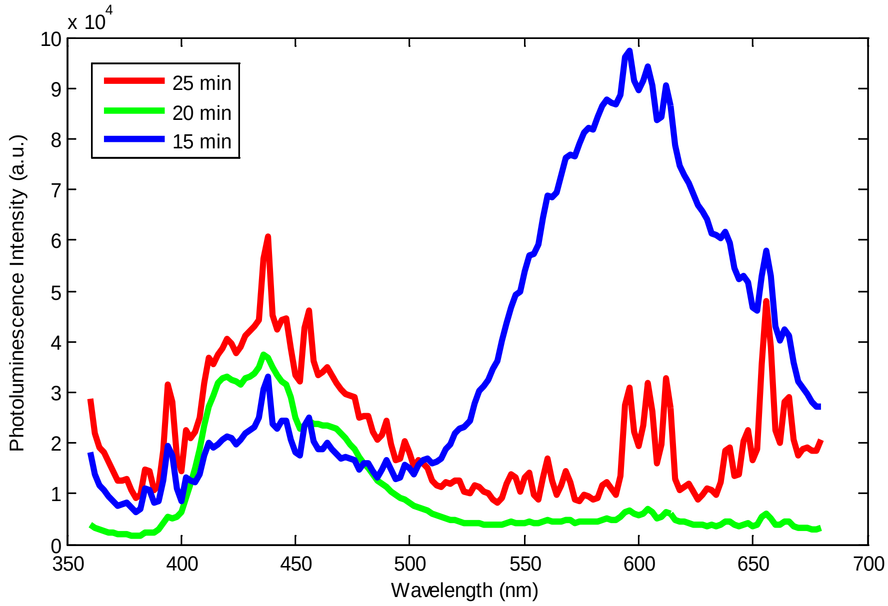

Figure (6) Photoluminescence spectrum of the PSi sample prepared with the assistance of green laser (50mW) at different etching times (15,20,25) min.

For this case, the best selected etching time = 20 min, thus, Eg_{psi} for λ at the peak intensity = 3.011 eV, the pore diameter for the case of green laser (50 mW) = 4.021 nm**.**

The above PL tests views and results can be discussed as follows:

1. The pore sizes produced by the assistance of blue lasers have the largest diameters even they are not evenly spread.
2. The band gap energies also differs in values but they are larger compared with the original bulk silicon (1.12 eV) as shown in AFM figures.
3. The inhomogeneity at some places are obvious in the PSi surface as illustrated in the AFM figures (7) and (8).

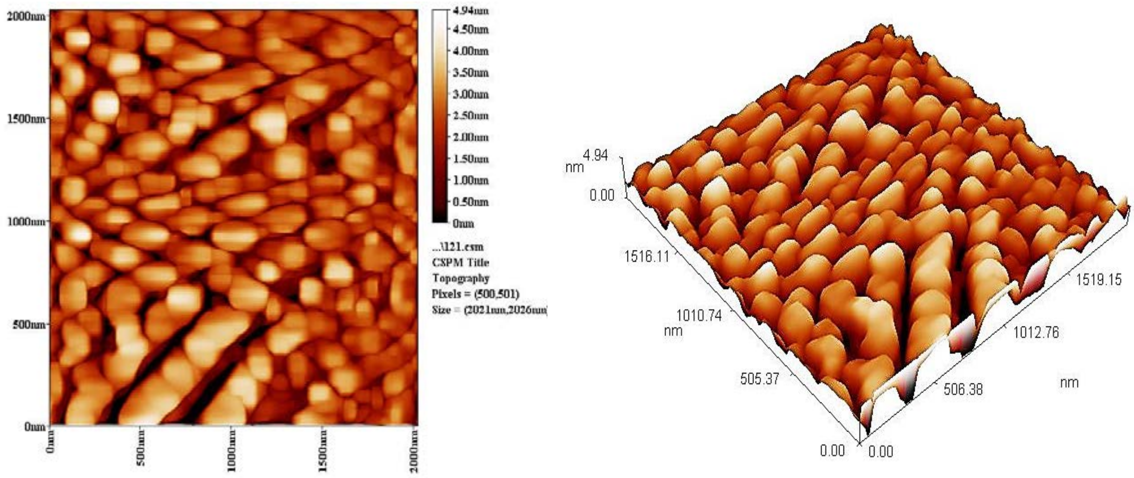

Figure (7): AFM image of porous silicon monolayer prepared at J=20 mA/cm^{2}etched under 15 min and blue laser=50mW

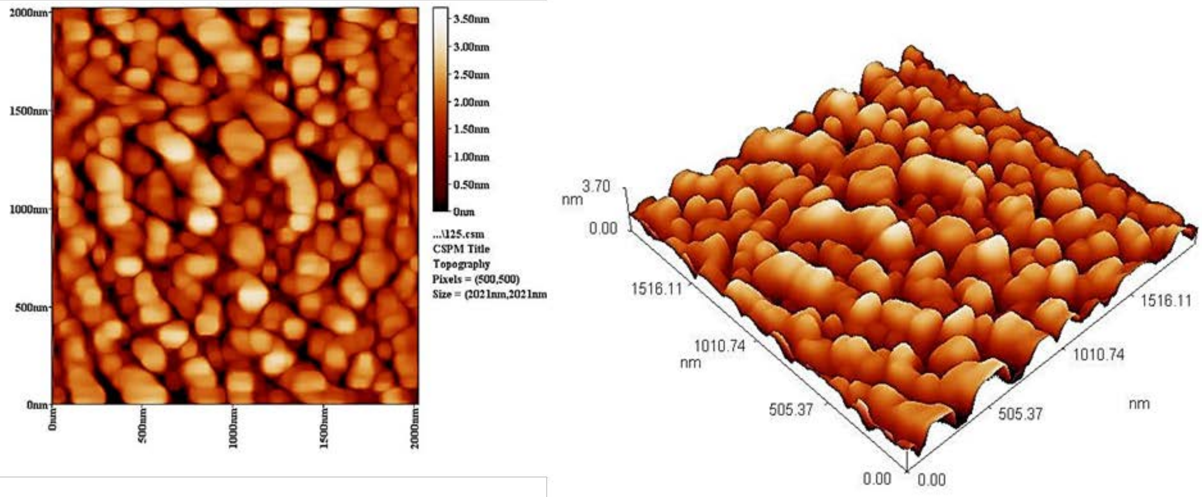

Figure (8): AFM image of porous silicon monolayer prepared at J=20 mA/cm^{2}etched under 15 min and green laser=50mW**.**

The AFM images show acceptable relative homogeneities after using blue and green assisting lasers respectively. The thicknesses are ranged between 3.70 nm up to 4.94 nm.

4. According to equation (1) and depending on Eg_{psi} measurements, Table (1) shows the refractive indices on the account of different band gaps obtained in this work.

Table (1) values of 2-refractive indices obtained from different measured bandgap.

Types of laser	**Eg_{psi} eV**	**n (ref. index)**
Blue (50mW,20min)	2.010	1.737
Green (50mW,20min)	3.011	1.540

The results of the refractive indices of both cases are in acceptable range of the PSi refractive indices.

Conclusions

1. Porous structures were prepared on n-Si single crystal wafer by a photo-electrochemical at a certain current density and etching time. The surface of the PS layer was investigated by the PL test and AFM .This study shows that PS layer thickness has a different value, depending on the method of calculation either experimentally or theoretically.
2. Results concluded from PL show that the energy band gap increased from 1.12 eV for the c-Si sample to, for instance, 3.011 eV for the PSi layer created. This result points out that the quantum confinement effect here is applied according to the new better dimension confinement of the particles. Thus, this would

produce a good recombination of the electrons and holes which results in high efficiency.
3. The refractive index of the PSi in both cases of laser wavelengths show good results lying in the acceptable range. Besides, more absorption of sun light can be obtained for the green laser sample applied for the purpose of using PSi as an ARC in solar cells.

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قياسات معامل الانكسار للسلكون المسامي المنتج بمساعدة نوعين من الليزرات

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الخلاصة :

تم تحضير عينات من السلكو ن المسامي على الوجه (n) من وجهي السلكون الخالص بعملية التنميش الضوئي-الكهروكيميائي اعتمادا على اعلومات متعددة وعلى ثبوت نسبة سائل التحلل الكهربائي بالمقدار ..
$HF:C_2H_5OH:H_2O$ (2:3:3) .... تتغير الخواص الفيزيائية والضوئية للسلكون المسامي بتغير هذه الاعلومات مثل تغير كثافة التيار و زمن التحلل والاطوال الموجية لليزرات .
في هذا البحث استعمل نوعان من الليزرات الدايودية ذوات 50 mW هما الليزر الازرق 473 nm والليزر الاخضر 532 nm وعند زمن التنميش المختار 15 دقيقة وكثافة تيار $20\ mA/cm^2$ للمساعدة في انجاز التفاعل .
ازدادت طاقة الفجوة للسلكون المسامي في بعض الحالات لاكثر من الضعف لتصل الى (2.9 eV) بدلا من (1.12 eV) . تم استغلال طاقات الفجوة المستحصلة من تفاعل نوعي الليزراتالمطبقة لحساب معامل انكسار السلكون المسامي اعتمادا على العلاقة التجريبية للعالم (فاندام). لوحظ ان مسامية الطبقة تتغير بتغير اعلومات التفاعل وهذا بدوره يغير من قيم معامل الانكسار ولذلك فان الحسابات اعتمدت على تثبيت اعلومات التفاعل خاصة الكثافة الكهربائية كي تتسنى المقارنة بين افضلية الطولين الموجيين لليزرات المستعملة.
طبق فحص PL وAFM على هذه النماذج لملاحظة مدى التجانس في مسامية طبقة السلكون ومدى خشونة سطحه اضافة الى مدى سمكه.
اظهرت النتائج توافقا جيدا جدا مع مدى قيم معاملات انكسار السلكون المسامي المستنبطة بطرق اخرى وظهر ان افضل معامل انكسار لطبقة السلكون المسامي التي تقل معها نسبة انعكاس الضوء وزيادة نسبة امتصاصه في الخلية الشمسية هي عند تطبيق الليزر الاخضر .