# The Effect of Laser Wavelength on Porous Silicon Formation Mechanisms

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## Abstract:

In this work, the effects of coherent radiation (Laser) with different wavelength and photon energy during the electrochemical etching process on the structural characteristics PS samples were investigated. The porosity values were measured by depending on the microstructure analyses and gravimetric measurements. Surface morphology, layer thickness, pore diameter, pore shape, wall thickness and etching rate were studied by depending on Scanning electron-microscopic (SEM) images.

**Keywords**: Porous Silicon, Illumination, SEM Images.

## 1. Introduction

Porous silicon (PS)is not a new material and it was first reported over 30 years ago during the electro polishing of silicon in aqueous hydrofluoric acid ,and has since been studied extensively [1], Photochemical etching(PC) [2,3] with laser provides an alternative method to produce and control the size and emission characteristics of PS. The photo electrochemical (PEC) is an ultra important method in industry of PS material because it is suitable for etching of n-Type and p-Type silicon in HF solution. This fact based on that the PEC etching process is collects between two ways (Electro and Photo chemical etching). *Juhasz and Thonissen* [4, 5] have reported that the illumination of n- as well as p-type PS during formation causes dramatic changes in the structure of layers. The n-type PS obtained under illumination by PEC etching process consists of layers of nanoporous silicon layer which covers a macro porous silicon layer with pores in the micron size range [6].

In PEC etching process the semiconductor is immersing in conductive electrolyte. The silicon is biasing as anode, when the Fermi level of the silicon electrolyte interface is within the band gap

as shown in figure (1), which shows the case of n-type silicon in contact with electrolyte [7].
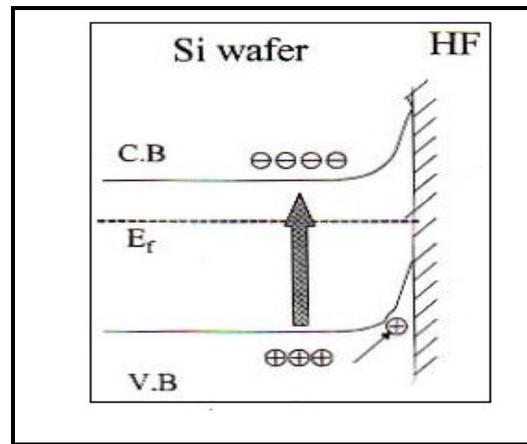


**Figure (1); Energy-band structure of n-typ silicon in contact with electrolyte [8]**

When a photon hits the silicon surface a number of process could be accurse, the photon could be reflected. Alternatively, it can be absorbed in the silicon. If the energy of the photon is large enough (more than ▯ 1.1 eV) it can excite electrons to the conduction band according to the important relation:

$$E = h\upsilon \Rightarrow E = \frac{1240}{\lambda_{nm}} ....  \quad 1$$

where $\upsilon$ (Hz) is the incident light frequency, $\lambda$ (nm) is wavelength, and E is the energy band gap in (eV).

The wavelength will limit the generating position of charge carrier; *Vincent* [10] has reported that the short wavelength ensures that electron-hole pairs are generated close to the Silicon / Solution interface. Therefore, a photo etching process can be much more effective at etching the thinner regions, while the charge carriers are generated deeply in the

silicon bulk to result primarily in excitation of the substrate as shown in figure (2).
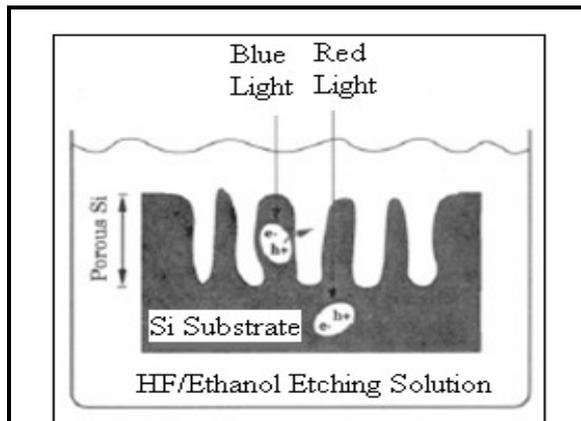


**Figure (2); the generation of charge carriers by different wavelengths [10, 11].**

## 2. Experiment:

Crystalline wafer of n-type Silicon with resistivity of 0.2 $\Omega$.cm, 508 µm thickness, and (111) orientation were used as starting substrates. The substrates were cut into rectangles with areas of 1 $cm^2$. The native oxide was cleaned in a mixture of HF and $H_2O$ (1:2). After chemical treatment, 0.1 µm-thick Al layers were deposited, by using an evaporation method, on the backsides of the wafer. Photo-electrochemical etching then performed in a mixture 48% (1:1) HF-Ethanol at room temperature by using a Pt electrode.
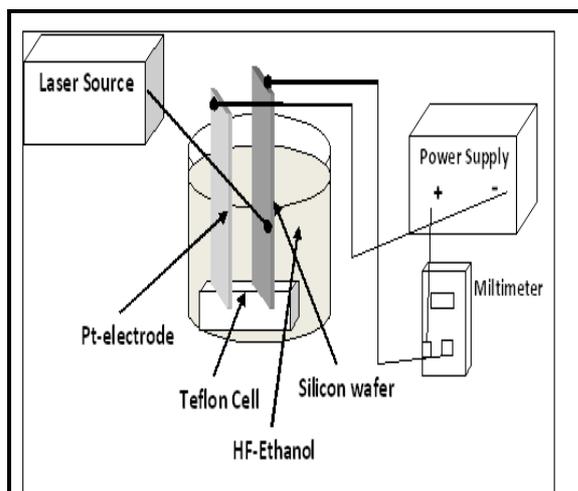


**Figure(3);Schematic digram depicts the PEC proces.**

Current of 40 mA/$cm^2$ was applied for 10 min .Samples were illuminated in two ways in the first, Infrared laser have wave length 810 nm with power 2 W , second by using green laser 514.5 nm and power 30 mW. The structure properties such as, porosity, surface morphology, layer thickness, pore diameter, wall thickness, pore shape and etching rate measured. These structural properties measured by scanning electron microscopy (SEM). Measurements were carried out in the School of Physics/Nanostructures and Optoelectronics Research Center (NOR)-lab, University Sian Malaysia (USM).

## 3. Results And Discussion:

In this paper, comparative study of morphological properties of PS samples produced by photo-electrochemical etching were attempted by using diode lasers have different wavelengths 810 nm and 514.5 nm , therefore all other etching parameters were kept constant, except the source of illumination. Figure (4) shows SEM images for formed PS  layer with two different laser wavelengths ,where sample A represented in figure(4a)which prepared by laser wavelength 514.5nm,while in figure(4,b) represent sample(B)  prepared with wavelength810 nm.
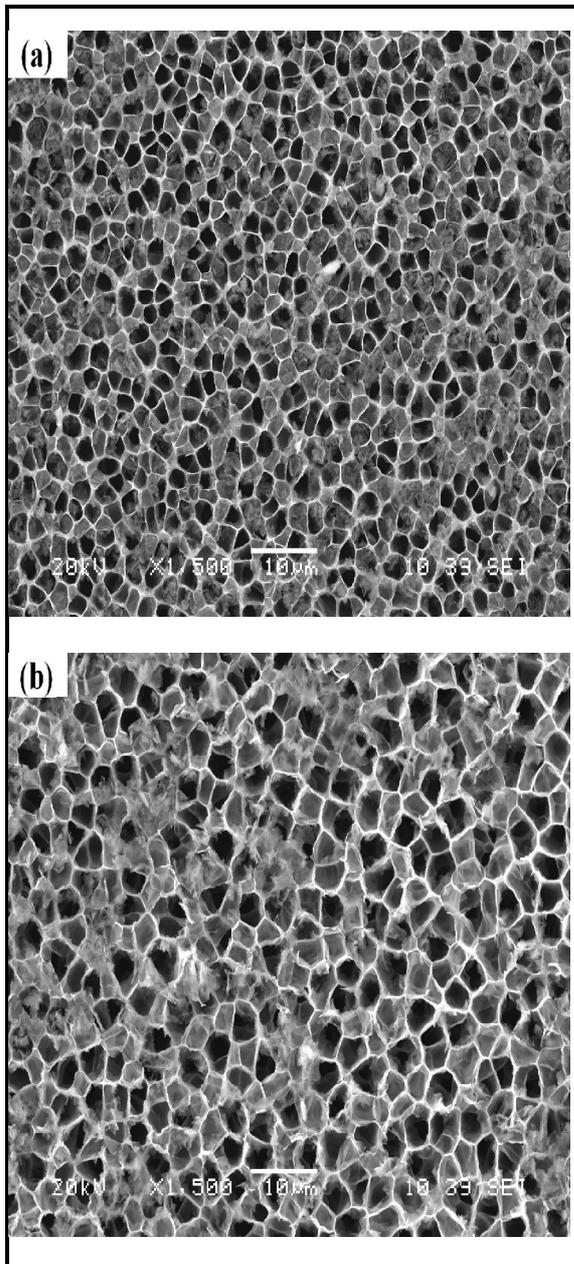
**Figure (4); SEM Image of formed porous silicon layer with different laser wavelengths at (a) 514.5 nm, (b) 810 nm.**

From figure (4) we could seen that some of pores appear blacken rather than others that because it deepest rather than other pores, with increasing laser wavelength the pore width will be increased .This attributed to sideways etching at the surface would become dominate and resulting a gradual erosion of the walls .From these figure we can emerged in some of results could be estimated in the flowing sentence:

### 3.1. Pore number and Pore width:

The number of pore in sample (A) which prepared by laser wavelength 514.5 nm is about $(11*10^8)$ pore/cm$^2$ and the pore number of sample (B) which prepared by laser wavelength 810 nm is about $(9*10^8)$ pore/cm$^2$. That largeness value number of porous for green laser rather than infrared laser is attributed to the fact that the green laser has energy band gap larger than infrared laser, where the photon energy was calculated from relation (1) is about 2.41 eV of 514.5 nm and about 1.35 nm for 810 nm laser wavelength, also we could observed that the pores which prepared by infrared laser have width larger than pores which prepared by green laser that because increasing etching rate with increasing laser wavelength make the pore to opening to each other sequent increase pore width and decreasing wall size which separated between pore and that lead to change pore shape where it triangular shape for 514.5 nm laser wavelength and cylindrical shape for laser wave length 810 nm. The pore width, and wall size could be estimated in Table 1

**Table (1); Shows pore width and wall size of PS prepared by different laser wavelength.**

| Diode Laser wavelength | Pore Width (µm) | Wall Size (µm) | Pore Shape |
|---|---|---|---|
| Green Laser (514.5nm) | 1.4-6 | 0.02-0.9 | Cylindrical |
| Infrared laser (810nm)) | 1.2-5.3 | 0.014-0.25 | Triangular |

## 3.2. Surface roughness:

The surface of PS samples which formed with high photon energy are rougher than samples which prepared by lower photon energy, that due to the number of pore of PS surface which prepared by green laser is higher than that which prepared by infrared laser.

## 3.3. Etching rate and layer thickness:

The etching rate can be calculated by using equation given by [12]:

$$V = \frac{d}{t} \quad .....\quad \boxed{2}$$

Where V (µm/min) is the etching rate, *d* (µm) is the layer thickness; *t* (min) is the etching time. We can calculate the layer thickness directly by using optical microscopy with resolution down to (600X).The etching rate values for formed PS prepared by different laser wavelengths given in Table (2).

From Table(2)we can observed that the etching rate increased with increasing laser wavelength that is attributed to two reasons ,first due to increase number of charge carriers which was necessary to dissolve one silicon atom along pore depth according to relation given by [13]:

$$N_P = \frac{P}{h v} \quad .... \quad \boxed{3}$$

Where, P is the power of the laser, *hv* is the energy of photon, and *v* is the frequency of the laser and $N_p$ is the number of photons irradiated on silicon wafer per unit time. According to relation (3) we can observed that the number of photon is inversely relation with photon energy. The density of electron-hole pairs (G) generated per unit time given by [13]:

$$G = \eta N_p \quad .... \quad \boxed{4}$$

$\eta$ is the quantum coefficient of Si,

Other reason to interrupt that increasing in etching rate with increasing wavelength that the etching rate is varying according to coefficient of absorption which is depend on the wavelength, where the absorption coefficient for 810 nm is about 12.82 µm and about 0.68µm for green laser that meaning the PS layer thickness for 810 nm is large so the etching rate is large rather than green laser.

## 3.4. Porosity

The porosity defines as the fraction of void within the PS layer .It is with thickness is most important parameters which characterize porous silicon. Porosity can determined easily by weighing measurements .The virgin wafer is first weighed before etching ($M_1$),then just after etching ($M_2$) and finally after dissolution of the whole porous layer in molar Na OH aqueous solution ($M_3$).The porosity *(P)* is given simply by the following equation [14]:

$$P\ (\%) = \frac{M_1 - M_2}{M_1 - M_3} \quad .... \quad \boxed{5}$$

From these measured masses, $M_3$ could be calculated directly after measured thickness without needed to remove PS layer according to the following formula [14]:

$$W = \frac{M_1 - M_3}{S \times d} \quad .... \quad \boxed{6}$$

where d is the density of bulk silicon ~2.3 g/cm$^3$ and S (cm$^2$) is the wafer area in which exposed to HF during etching process which is about 0.5 cm$^2$ for two cases, Table (2) shows the value of porosity of two different laser wavelengths, we can observed that infrared laser has larger value of porosity rather than green laser due from increase voids between walls subsequent increasing porosity

| Table (2); Shows the value of etching rate, layer thickness and porosity of PS prepared by two different laser wavelengths. | | | |
|---|---|---|---|
| **Diode Laser wavelength** | **Layer thickness (µm)** | **Etching rate (µm/min)** | **Porosity %** |
| Green Laser (514.5nm) | 20 | 2 | 51 |
| Infrared Laser (810nm) | 24 | 2.4 | 72 |

## 4. Conclusion

The obtained results show that the structural properties of PS layer depend upon the wavelength of employed illumination source. In case of implying infrared laser, the porosity, and pore diameter are higher than these measured in the green laser. The PS surface roughness and wall size

in the case of green laser is larger than that samples which formed by infrared laser.

## Acknowledgement

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# تأثير الطول الموجي لليزر على آليات التكوين للسليكون المسامي

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## الخلاصة:

في هذا البحث تم دراسة تأثير الإشعاع المتشاكه (الليزر) بأطوال موجية وطاقة فوتونية مختلفة خلال عملية القشط الكهروكيميائي على الخصائص التركيبية للسليكون المسامي. ان قيم المسامية تم قياسها بالاعتماد على التحاليل التركيبية الدقيقة وبالطريقة الوزنية. طبوغرافية السطح، سمك الطبقة، قطر الفجوة، شكل الفجوة، وسمك طبقة الجدار بين الفجوات وكذلك معدل القشط تم قياسها بالاعتماد على تحليل صور المجهر الالكتروني الماسح