

## Preparation and Characterization of Porous Silicon Prepared by Electrochemical Etching

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### ABSTRACT

Porous silicon (PS) layers were formed on p-type silicon (Si) wafers by using electrochemical etching method. The influence of varying etching time in the anodizing solution, on structural and optical properties of porous silicon has been investigated. Additionally, the thickness and porosity of the layers were measured using the gravimetric method. The surface morphology was studied by Scanning Electron Microscope (SEM). Finally, the optical properties of porous silicon on silicon substrates were investigated by employing photoluminescence (PL).

**Keywords:** Porous silicon, Electrochemical etching, Porosity, Morphological Properties, Photoluminescence.

### تحضير ودراسة خصائص السليكون المسامي المحضر بطريقة التنميش الكهروكيميائية

#### الخلاصة

تم تشكيل طبقات السليكون المسامي على شرائح السليكون نوع p باستخدام طريقة القشط الكهروكيميائية. فحص تأثير اختلاف زمن القشط على الخصائص التركيبية والبصرية للسليكون المسامي. بالإضافة إلى ذلك فإنه تم احتساب السمك و مسامية الطبقات باستخدام الطريقة الوزنية. درست طبوغرافية السطح باستخدام المجهر الماسح الألكتروني SEM أخيراً لقد تمت دراسة الخصائص البصرية للسليكون المسامي باستخدام طيف اللعان الضوئي PL.

### INTRODUCTION

Porous silicon (PS) was discovered in 1956 by Uthir [1] while performing electropolishing experiments on silicon wafers, using an electrolyte containing hydrofluoric acid (HF). Porous silicon (PS) can be considered as a silicon crystal having a network of voids on it. The nanosized voids in the silicon bulk form a sponge-like structure of pores and channels surrounded by a skeleton of crystal-line silicon nanowires [2]. The interest in porous silicon has increased greatly over the

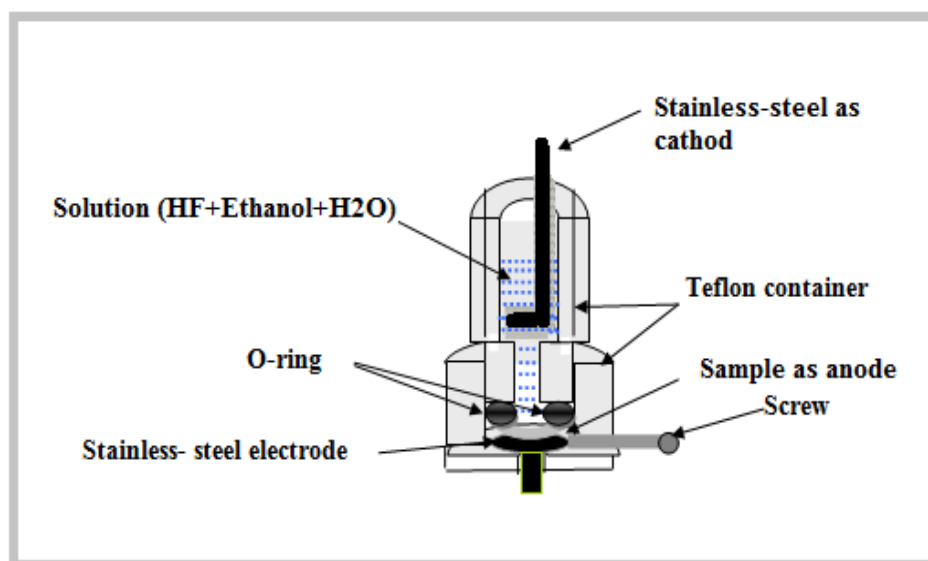
last decades, mainly due to its photoluminescence properties and the potential applications, which arise from these [3,4]. Technological application of porous silicon (PS) as a light emitter would have a significant impact on numerous technologies such as light emitting devices [5] microcavities [6], waveguides [7] and solar cells [8]. Porous silicon (PS) is an interesting material for gassensing [9]. In the 1970s and 1980s, interest in PS increased because its high surface area was found to be useful as a model of the crystalline silicon surface in spectroscopic studies [10]. In this report, PS formation was obtained by electrochemical dissolution of silicon wafers in aqueous or ethanoic HF solutions. The morphology and size of pores which produced by these techniques might be controlled by varying different conditions such as silicon doping, HF concentration, power density of the laser used and current densities, etc... [11]. The structural properties were studied by FESEM and the optical properties investigated by employing photoluminescence (PL). This paper investigated the effects of etching time as variable factors simultaneously on the physical, optical properties of PS.

### EXPERIMENTAL WORK

Electrochemical etching technique is used in this study to prepare PS layer. A commercially available p-type <111> oriented silicon wafer of thickness ( $508 \pm 15 \mu\text{m}$ ) with (1.5 - 4)  $\Omega\cdot\text{cm}$  resistivity has been used. The silicon wafer has been cut out into small pieces in dimensions of ( $2 \times 2 \text{ cm}$ ) before starting etching process. After the cleaning, the silicon wafers were immersed into hydrofluoric acid (HF) aqueous solution. The silicon (Si) sample was placed in the bottom of cylindrical Teflon cell and fixed by an stainless steel plate as a backing material in such a way that the current required for the etching process, could pass from bottom surface to the top of the polished surface via the electrolyte. A stainless steel rod represents the cathode which was placed perpendicular to the Si surface at a distance of 1 cm. The solution for electrochemical etching was HF 48 % :  $\text{H}_2\text{O}$  :  $\text{C}_2\text{H}_5\text{OH}$  99 %, in the ratio 1:1:1 respectively. Bubbles were observed during the etching process and the wafers were etched for current density 20  $\text{mA}/\text{cm}^2$  at different etching time 5, 7, 10 and 15 min, after which they rinsed with ethanol and dried in the ambient. The porous layer was formed on the mirror-like side of wafer. The porosity of PS layers has been determined by using the gravimetric method according to the following equation [12]:

$$y = \frac{m_1 - m_2}{m_1 - m_3} \quad \dots(1)$$

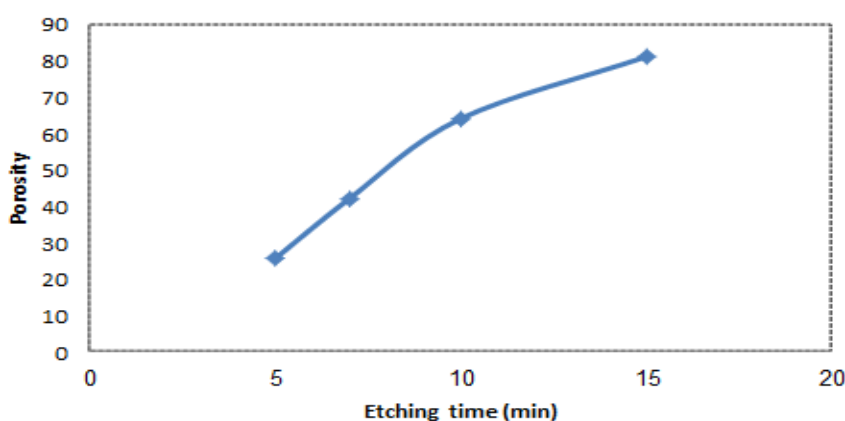
Where  $y$  is the porosity,  $m_1$  and  $m_2$  are the weight of the silicon substrate before and after the etching process respectively, and  $m_3$  is the weight after removing the porous silicon layer in molar of KOH with 30 min. The photoluminescence measurement was done by using He-Cd laser at wavelength of 335 nm with a low laser power density of nearly  $10 \text{ mW}/\text{cm}^2$  in the ministry of sciences and technology in Iraq. Figure (1). Shows a schematic diagram of experimental set-up for electrochemical process.



**Figure (1) Experimental set-up up for electrochemical process.**

**RESULTS AND DISCUSSION**

As mentioned above, the porous layer of silicon was fabricated by means of the electrochemical etching in HF solution. Figure (2) shows the relationship between porosity and etching time of prepared PS layer at different etching time (5, 7, 10 and 15min). From this Figure, we can see that the values of porosity are increasing with increasing of etching time. This result is ascribed to the increasing of the number and width of the pores with increasing of etching time as showing in Figure (2).

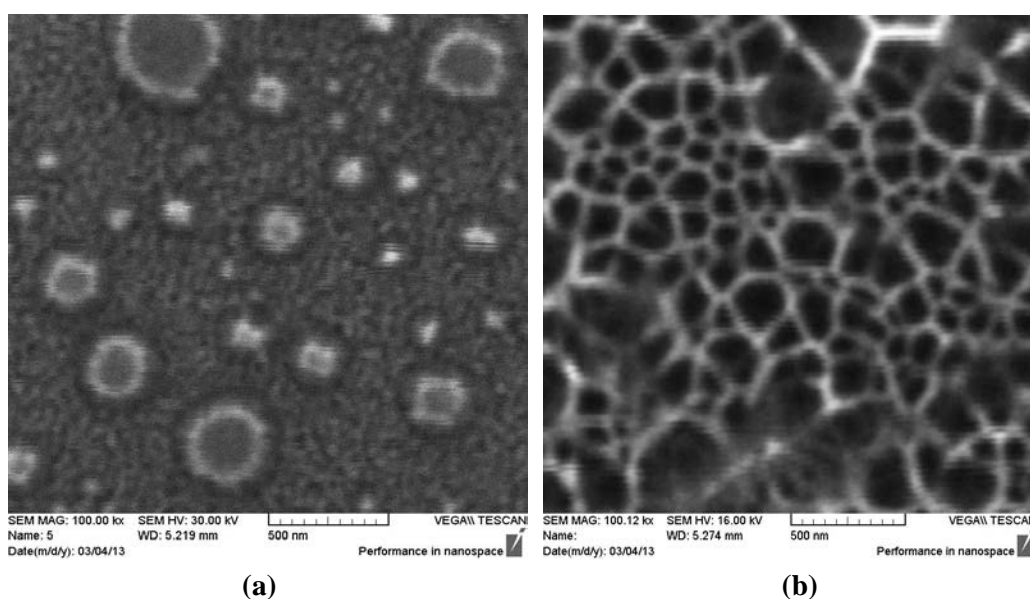


**Figure (2) The relation between porosity and etching time.**

Figure (3) shows a typical SEM image of the etched surface prepared under current density of 20 mA/cm<sup>2</sup> and under concentration (HF:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O) in the ratio (1:1:1) at different etching time of 10 and 15 min with pore size ranging from 29.6 nm to 225.2 nm. As shown in both images, the bright regions represent the Si

structures while the dark regions represent the pores. It is quite clear from Figure (3a) that when an etching time of 10 minutes is used fairly medium sized pores are formed, the pores are surrounded by thick columnar structure network of silicon walls. On the other hand, when the etching time is increased to 15 minutes Figure (3b) it can be seen that diameter increase of the pores are formed all over the surface region of the etched silicon layer. Interestingly, increasing the etching time accompanied with increasing the porosity of porous silicon layer followed by decreasing in the silicon structure.

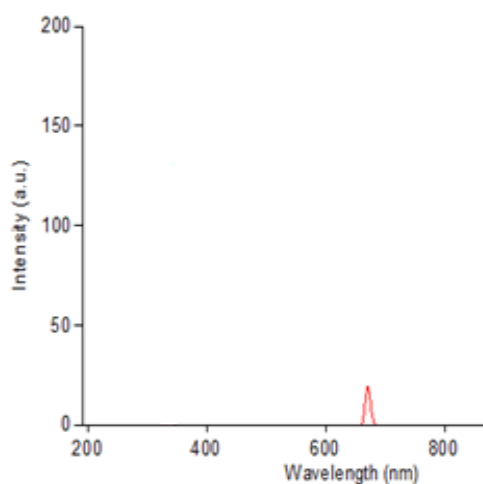
The pore size distribution is relatively uniform and the columnar walls are thin. The figure clearly indicates the sponge like structure of porous silicon layer. As - prepared layer has pores and trenches with various sizes and shapes. We can note from this images that the pore size increase with increasing of etching time.



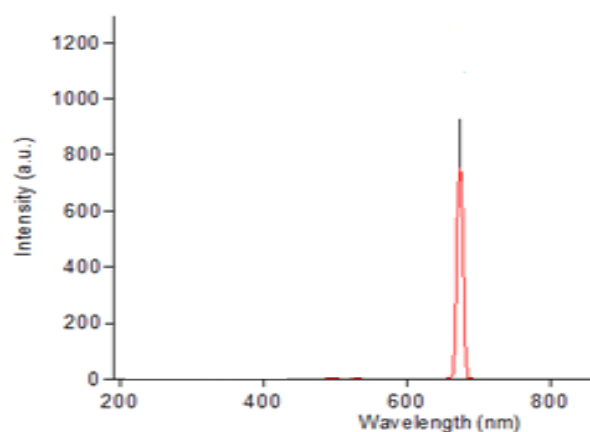
**Figure (3) SEM image (top - view) of the porous sample prepared by etching time: a) 10 min and: b) 15 min.**

Figure (4) shows Photoluminescence emission spectra of the p-layer of the porous samples which prepared in electrochemical etching process at different etching times (10 and 15 min) at fixed etching current density of  $20 \text{ mA/cm}^2$  under etching concentration of (1:1:1). The PL spectra was performed by exciting the synthesized porous layer with a (He-Cd) laser at a wavelength of (335)nm in order to include the widest range of crystallites to be excited as shown in Figure (4 a, 4b) which corresponds to etching time of (10 and 15) min, respectively. All the figures showed that the PL curves have sharp peak intensity at different wavelengths which referring to a porous layer with nanosized [13]. In case of p-porous silicon produced by a 10min etching time as shown in figure (4a), the obtained PL spectrum has a peak wavelength position of (672)nm and energy gap of porous silicon layer peak position of (1.84) eV. Compared to other case as shown in Figure (4b) where the sample is prepared at etching time 15 min, significant changes of (PL) peak position, where it is shifted towards higher wavelength peak position of (675) nm and hence the energy gap of porous silicon layer peak is about (1.83) eV. The variation of etching time lead

to Red and blue shift of the emitted PL this may due to the information of silicon nanosize at different size in the layer [14, 15].



(a)



(b)

**Figure (4) Photoluminescence spectrum of the porous sample prepared by etching time: a) 10 min and: b) of 15 min.**

## CONCLUSIONS

In summary, PS samples were prepared by electrochemical etching method under different etching times. We have studied the dependence porosity of samples on the etching time. The results show that the porosity increase with increasing etching time. So the surface morphology of the porous layer will be change with increasing porosity were the (SEM) image refers to the pore size increase with increasing of etching time. And from (PL) curves we can note that the peak wave length position is change with increasing of etching time were by increasing the etching time the peakis shifted towards higher wavelength peak position.

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