

## Characterization of (nanostructures silver/silicon nano porous) active substrates for surface enhanced Raman scattering (SERS) as a function to porous silicon parameters

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### Abstract

Electrochemical etching processes at different current densities were used to prepare nano porous silicon with different porosities. A series of nanostructures silver/ nano porous silicon (NAg/NPSi) active substrate were prepared by an immersion-plating method. Through controlling the current density the surface-enhanced Raman scattering (SERS) behaviors to cytochrome c (CY) dye were contrastively studied, for a concentration of ( $10^{-5}$  M), The (SERS) behavior was attributed to the size of the deposited silver nanoparticles on porous layer. The sensitivity of SERS signal increases with increasing the porosity of porous sample.

دراسة خصائص الشرائح النشطة (السيلكون المسامي النانوي المطعم بجسيمات الفضة النانوية) لتعزيز استجابة رامان المعززة سطحيا كدالة لمعاملات السيلكون المسامي

### الخلاصة

في هذا البحث تم استخدام طريقة التتميش الكهروكيميائي وبتيارات مختلفة لإنتاج سيلكون مسامي نانوي بمساميات مختلفة. استخدمت السيلكون المسامي لإنتاج القواعد النشطة لتعزيز حيود رامان السطح واستخدمت هذه القواعد للكشف عن المواد الكيماوية مثل صبغة الكريبتوسيانين عند التركيز المخفف ( $10^{-5}$ ) مولاري ووجدت إشارة تعزيز حيود رامان للسطح تتحسن مع زيادة مسامية السطح للسيلكون المسامي.

### INTRODUCTION

Raman spectroscopy (RS) is an important analytical process for chemical and biological analyses due to excellent structural information content. However, applicability of this technique was restricted because of an extremely small Raman scattering (RS) cross section, thus preventing the possibility of low chemical concentration detection. The renewed interest in Raman spectroscopy has been emerged

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due to the observations of enormous enhancement of Raman signal for metallic molecules adsorbed on surfaces with nano scale sizes [1–3]. This so-called the surface-enhanced Raman scattering (SERS) phenomenon opens a wide range of new possibilities of the Raman technique for trace chemical analyses, and biomedical applications [4–7]

Porous silicon (PSi) was used as bases for SERS-active substrate preparation in several recent works [8-14], namely (NPSi) was investigated as a template for silver nanostructures deposition. Due to its large surface area of about ( $500 \text{ m}^2/\text{cm}^3$ ) and open porous structure, this semiconductor material allows to obtain highly sensitive SERS substrates. This can be achieved by silver nano particles synthesis on porous silicon surface [8–12] or homogenous coating of pore walls with metal layer or inside the pores [13].

The most critical aspect of SERS is the development of active substrate (NAg/NPSi). These substrates need not only to have a rough nano scale features, but also should demonstrate it in an way of preparation and compact size. The aggregated silver colloids can be easily prepared and often provide the strong Raman enhancement, especially when the pores size in the nano regime. Large number of new SERS-active materials have appeared during the last decade due to progress in nano sciences and nano technologies. The growing interest to the nanofabrication is obvious since the SERS enhancement depends on the size, shape, and inter spacing of noble-metal nanoparticles [15]. There are several methods for the formation of such surface-confined nanostructures, including electron-beam lithography [16], nano sphere lithography [17], and films over nano spheres [18]. However, practically all these materials are costly and require special technique and trained personals for the fabrication.

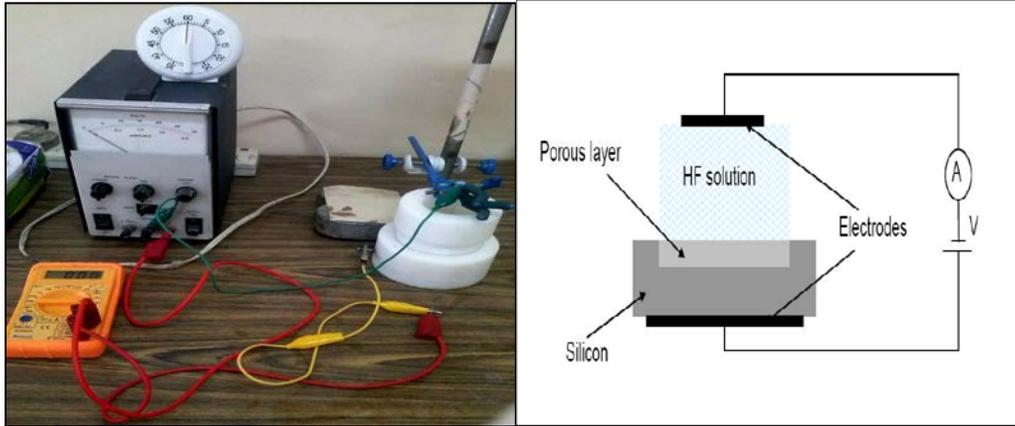
In this work, we prepared nano porous silicon by using electro chemical etching process of p-type. The active substrate was prepared by using the dipping process of nano porous silicon in silver nitride solution, and study the SERS characteristics of (NAg/NPSi) active substrate as a function to porous silicon parameters.

### **Experimental details**

Nano (PSi) structure was prepared by electrochemical etching of p-type Si (100) plates with resistivity ( $10 \Omega \text{ cm}$ ). The etching process was carried out in special designed cell fabricated from Teflon. The etching solution is a mixture of HF and ethanol (1:1), the concentration of HF is about 24%.

The set-up consists of (D.C) power supply as a current source; ammeter and aqueous HF acid in Teflon container with ethanol to prevent or minimize the hydrogen bubbles during anodization.

A platinum ring was used as the counter electrode. The series of psi samples was prepared by changing the etching current density (10,15,20,25)  $\text{mA}/\text{cm}^2$  and the etching time is about 20 min. figure(1) illustrates the electrochemical etching set-up. The porosity was determined gravimetrically.



**(a) (b)**  
**Figure (1): The electrochemical etching set-up (a) photograph (b) schematic diagram.**

The active substrate was prepared by the silver deposition on the surface of PSi, this process was carried out by the immersion plating. PSi plates were incubated into the ( $10^{-2}$  M) aqueous  $\text{AgNO}_3$  solution for different fixed dipping time of (10) min. the prepared Silver-coated PSi (active substrates) (Ag-PSi) were thoroughly rinsed with ethanol, and then dried in air.

Samples for the SERS activity measurements were obtained by the incubation of Ag-PSi for (5)min in solution of crptocyanen (CY) dye. Which was used as an analyte in this study. The concentration of this dye is about ( $10^{-5}$ M) and its prepared by dissolving the specific weight in triply distilled water. The molecular weight of (CY) dye is about (480.39g/mole). The equation (1) was used also to prepare the testing concentration.

$$M = \frac{W(g)}{mW(\frac{g}{mole})} * \frac{1000}{V} \quad \dots(1)$$

Where

(W) Dye weight , (Mw) Molecular weight and (V) The size of the solution.

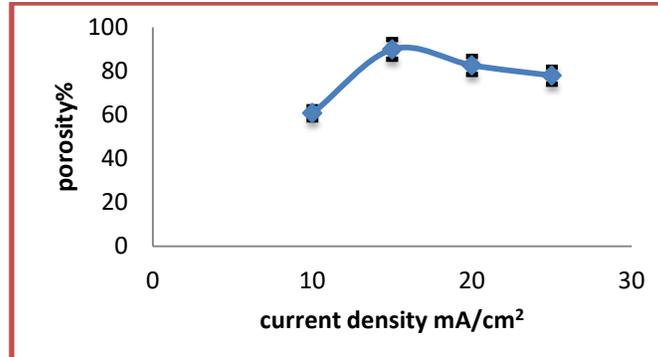
The field- emission scanning electron microscopy measurement (FE-SEM) type(JEOL-JSM-7800F) and made in Japan. The resulted Raman spectra were measured by using the (Renishaw Raman scope 2000) using (532nm) line of  $\text{Ar}^+$ -ion laser for excitation.

## Results and discussion

### Porosity of nano porous silicon.

The porosity of the porous layer is the most important parameter which characterizes the PSi. The porosity is defined as the function of void space within the porous layer. The porosity is strongly dependent on the anodization conditions. These conditions include

current density, etching time. Figure (2) show the porosity of (NPSi) sample as a function to etching current density, orientation and etching time. The experiment was carried out using (10  $\Omega$ . cm) (100) orientation (p-type) silicon substrate in 24% concentration of HF acid in mixing ratio (1:1) HF: C<sub>2</sub>H<sub>5</sub>-OH. As shown in figure (2) the increasing of etching current density will lead to increase the porosity to a maximum value of 90% at etching current density of 15 mA /cm<sup>2</sup>. The further increase of the etching current density 25 mA /cm<sup>2</sup> will make the porosity value decrease in small amount 78% at (like a saturation case). The increase of the porosity with etching current density may be due to increase the numbers and diameter of pores inside the nano PSi layer. This variation in porosity inside the pores layer is in a good agreement with the results of [A.Yu. panarin(*etal*)] in [19]; they reach to the fact that the increasing of etching current density from 20 mA/cm<sup>2</sup> to 40 mA /cm<sup>2</sup> lead to increase the mean pore diameter from (15-25 nm), and they found also that the current variation may lead to change the morphology of porous silicon layer from sponge-like structure to columnar- like stricture which consists of tiny diameter of pores from (1 nm to several nm) and considerably higher surface area. The increasing of the anodization current density up to (15 mA /cm<sup>2</sup>) on can easily notice that the porosity of the (NPSi) layer at high current density reaches to saturation state. A saturation case is established when a steady state is reached between silicon dissolution process and the number of the number of (h<sup>+</sup>) holes in the silicon regions. This may increase the energy gap of the resulting (NPSi) layer to a large value greater than that of the crystalline silicon.

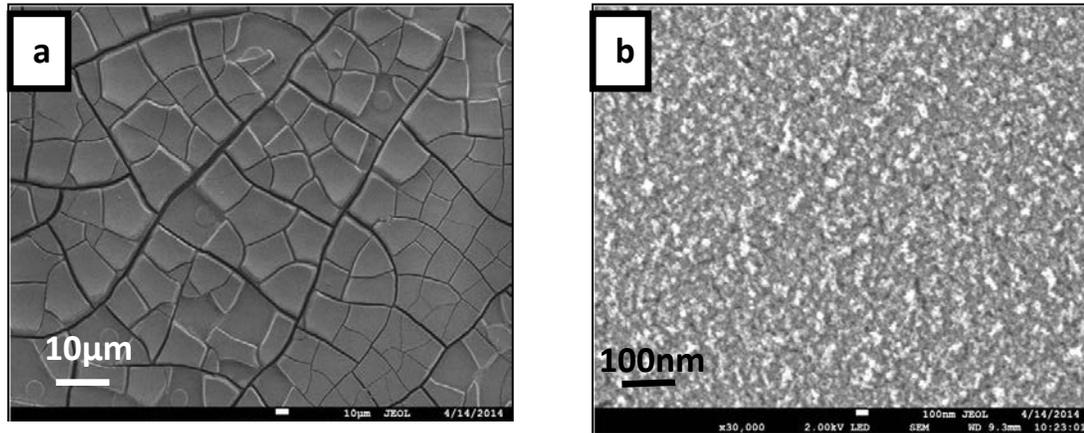


**Figure (2): Shows the variation of PSi layer porosity with etching current density for (100) p-type at fixed etching time (20 min) by electro chemical etching process.**

### **Surface Morphology of (as-prepared) nano porous silicon**

The morphological aspects of the (NPSi) surface like pore width; pore shape and silicon nano spacing between adjacent pores are strongly dependent on the preparation conditions. The experimental conditions like etching current density, etching time; type of silicon wafer on the surface morphology images was studied. Figure (3b); shows the surface morphology of (100) p-type (NPSi) layer (top-view). The (NPSi) samples were prepared under 20min, 24% HF acid concentration with fixed etching current density of 15 mA/cm<sup>2</sup>. It was found that the resultant porous structure as show in figure(3a), has a

mud-like structure consists of connected and non-connected trenches, figure(3b); shows a magnified FE-SEM image down to nano scale region, Inside each muds. This image shows that a pore-like structure with a fine sizes a lined also in random direction in addition to very small trenches in random direction. The sizes of the pore width in the rang (20-50 nm). this non-uniformity of silicon nano sizes may be refer to non-uniformity in the holes( $h^+$ ) distributions along the silicon channel[20].



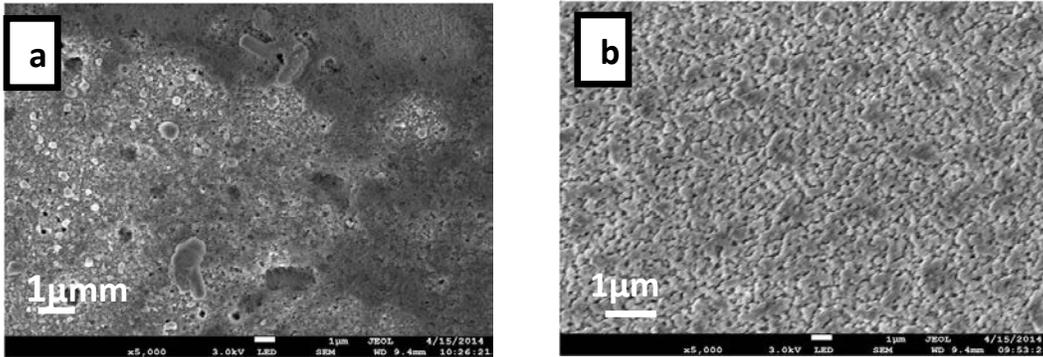
**Figure(3): FESEM image of p-type(100) porous silicon surface prepared by electrochemical etching conditions of 15 mA /cm<sup>2</sup> for 20 min etching tim at different magnifications (a)300 (b) 30,000 .**

#### **The effect of porosity on porous layer**

The main parameter of porous structure is the porosity of the PSi layer, the effect of this parameter on the morphology of on the SERS- active substrate is illustrated in figure(4a,b) for p-type porous samples of different porosities 93% and 60%. For both samples the dipping time in AgNO<sub>3</sub> solution is about 10 min.

Figure(4 a,b), shows the FE-SEM image(top-view) of two silvered (NPSi) n-type(100) with different porosity 30% low porosity level and 80% high porosity level which corresponded to 10mA/cm<sup>2</sup> to 15mA/cm<sup>2</sup> etching current density respectively. We can conclude the following explanation that the increase of etching current density causes increase of sample porosity and average pore size. Increase of current density defines the amount of hole (per unit area) directed to the silicon surface and consequently, in fluencies the pore width and larges total surface area of PSi. The increasing of etching time will improve the nano structure film (NPSi). The pores so a big and enough nanoparticles can form a complex structures. At high porosity sample we can see a densely structured nano aggregates form of silver nanoparticle, compared with the low porosity sample the silver film does not fully covered the porous layer and the silver aggregation is not fully connected between them. There as one of this morphology may be also related to the dangling bonds (Si-H) bonds, where the high porosity (PSi) sample has a high density of dangling bonds. This type of bond play an important role in silver reduction process during immersion of PSi into AgNO<sub>3</sub> solution and can acts as a

nucleation sites. This result is in good agreements with [21] where porous sample has high porosity and dense silver nanoparticle aggregate on its surface after silver deposition.

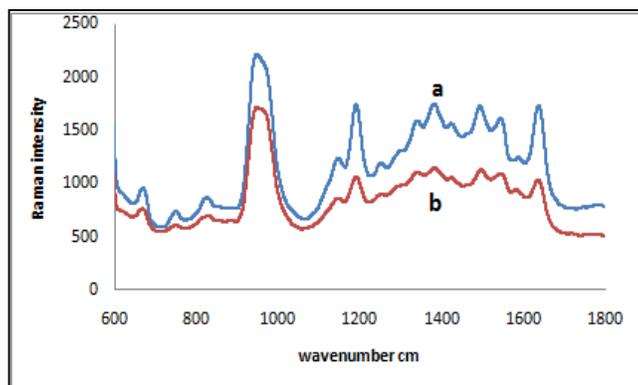


**Figure(4): FESEM images of silver layer deposited on porous silicon from  $(10^{-2} \text{ M})$   $\text{AgNO}_3$  solution at fixed dipping time for p-type(100) porous sample of different porosities(a) high porosity 93%(b) low porosity 60%.(active substrate)**

#### **Effecting the etching current density on activity of porous silicon/ Ag nanostructure.**

the SERS activity of PSi/Ag nanostructures active substrate is depended on the morphology of the PSi layer like porosity, pore sizes and layer thickness [21], the influence of different etching current density on the morphology of the initial (PSi) samples and SERS efficiency have been investigated. Raman spectroscopy performed on aqueous solution  $10^{-5} \text{ M}$  of cyanine dye CY-5-OCH<sub>3</sub> dissolved in high purity ethanol. Two PSi /Ag nanostructures active substrate was employed in the process. The p-type (100) orientation PSi samples have different porosities 60% and 93% at etching current density ( $10 \text{ mA/cm}^2$ ) and ( $15 \text{ mA/cm}^2$ ) respectively.

Figure (5) illustrates direct comparison of SERS spectra of cyanine dye CY-5-OCH<sub>3</sub> dye molecule at fixed dipping time 10min in  $10^{-5} \text{ M}$   $\text{AgNO}_3$  solution. For p-type (100) orientation two PSi samples of different porosities 60 % and 93 %. The spectra show a significant peaks at specific wave number ( $1160, 1350, 1500, 1550 \text{ cm}^{-1}$ ). These peaks is in a good matching with that peaks obtained by (M.V. [Chursanova(etal) ] [ 21].



**Figure(5):**Raman spectra of  $10^{-5}$ cryptochyanen on (100)p-type/Ag sample with silver nanoparticle deposited from  $10^{-2}$   $\text{AgNO}_3$  deposition time 10min for two porous sample with two different current density (a)  $10 \text{ mA/cm}^2$ , (b)  $15 \text{ mA/cm}^2$ .

### Conclusion

Electro chemical etching process for p-type porous silicon of high porosity regime of 60% and 93% lead to prepare nano porous silicon a primary substrate to prepare (Ag/Si-NPA) active substrate for (SERS). The increasing of porous silicon porosity lead improve the sensitivity of the active substrate for SERS signal especially at peak  $(1160, 1350, 1500, 1550) \text{ cm}^{-1}$ .

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