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Preparation and Characterization of Nano Porous Silicon for Chemical Detection Applications

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ABSTRACT

In this research Photo-electrochemical etching process was used to prepared nano porous silicon from n-type Si. The characteristics of Silvered porous silicon samples (active-substrate), was studied as substrates in terms of surface-enhanced Raman scattering (SERS) phenomena. Maximum of (SERS) enhancement for Cresyl violet (CV) dye was obtained. The active substrate was prepared by the immersion plating from the water solution of $AgNO_3$ with the (10^{-2}M) concentration during (5min). The relation between the etching parameters, morphology of porous silicon surface and its SERS efficiency after silver deposition is examined .We show that the nano (PSi) allows the formation of a film with close-packed silver nano crystals, which possess strong surface enhancement properties.

Keywords: Electroless deposition; Silver nitrites; nano porous silicon; Surface-enhanced Raman scattering (SERS).

تحضير وتحديد خصائص سيلكون مسامي نانوي لتطبيقات الكشف الكيميائي

الخلاصة

في هذا البحث تم استخدام عملية التنميش الضوء- الكهروكيميائية لتحضير سيلكون مسامي نانوي من نوع المانح .ان لخصائص العينات السيليكونية المسامية الفضية (الشريحة النشطة) ، قد تم دراستها كدالة لظاهرة سطح تعزيز رامان المتشت (SERS). وقد تم الحصول على اعظم تعزيز لتشتت رامان السطحي كان لصبغة الكريستال البنفسجي (CV). ان الشريحة(المنشطة) تم تحضيرها وذلك بغمر شريحة السيلكون المسامي النانوي في المحلول المائي لملح نترات الفضة وبتركيز(10^{-2}) مولاري ولفترة (5 دقائق). تم دراسة العلاقة بين معاملات التنميش لطبوغرافية السطح وكفائة التعزيز لحيود رامان السطحي ووجد ان السيلكون المسامي النانوي المطعم بجزيئات الفضة النانويه يمتلك أعلى تعزيز وبالتالي أحسن كشف للصبغات العضوية.

الكلمات المرشدة : الترسيب بدون اقطاب , نترات الفضه, سيلكون مسامي نانوي, تعزيز استطارة سطح رامان

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INTRODUCTION

Surface-enhanced Raman scattering (SERS) is a sensitive technique allowing vibrational spectra from individual molecules to be measured.[1-3] Among single-molecule spectroscopes, it provides much more detailed information as compared to the broad fluorescence spectra. Raman spectroscopy provides highly resolved vibrational information and although the molecular Raman cross sections are much smaller than the fluorescence ones, the SERS mechanism can enhance the Raman efficiency making it competitive in terms of signal intensity.

The increase of the Raman scattering efficiency is attributed to two fundamental effects. The main one is concerned with the enhancement of the electromagnetic (EM) fields localized at the edges of metallic particles after excitation of surface Plasmon's at resonance conditions, which can lead to giant EM enhancement up to factors of (10^{11}–10^{12}) [4].

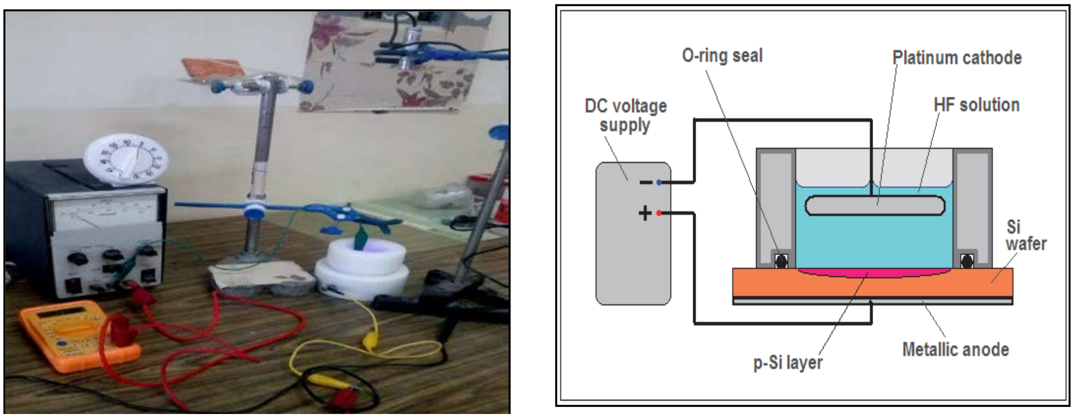
Porous materials were used as bases for SERS-active substrates preparation in several recent works [5–11], namely porous silicon was investigated as a template for silver nanostructures deposition. Due to its large surface area and open porous structure, this semiconductor material allows to obtain highly sensitive SERS substrates. This can be achieved by silver nanostructures synthesis on porous silicon surface [5–9] or homogenous coating of pore walls with metal layer [10].

Morphology of the final SERS-active substrate film depends on the porous silicon substrate structure, which, in its turn, is determined by silicon etching conditions [12].

In this work we prepare silver nanoparticles spontaneously from their aqueous solution. Silvered porous silicon (active substrate) was examined for detection of chemical compound as a function to dipping time.

Experimental Details

Nano (PSi) structure was prepared by photo-electrochemical etching of n-type wafer (100) plates with resistivity(10 Ω 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 series of pore Si samples was obtained at values of different current density(J) of (16mA/cm^2) and variable etching time of (5, 7,10 and15min). The illumination was carried out by using diode laser source as an illumination sources. A diode laser with wavelength (405 nm) and fixed output power (40mW/cm^2) the illuminated area is about (0.8cm^2) was used . and schematically shown in figure (1).



(a) **(b)**

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

The active substrate was prepared by The silver deposition on the surface of (PSi). $AgNO_3$ (High purity 99.99%) of (169.87g/mol) molecular weight triply distilled water was used to prepare solution of (10^{-2}M). The required volume of the water was calculated based on the following equation.

$$molary = \frac{w(g)}{mW(\frac{g}{mole})} * \frac{1000}{voloum} \qquad ....(1)$$

This process was carried out by the immersion plating of (PSi) plates into the (10^{-2}M) aqueous $AgNO_3$ solution for different time (10, 15 and 20) 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 Cresyl violet (CV) dye. which was used as an analyst 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 (CV) dye is about (361.74 g/mole) .

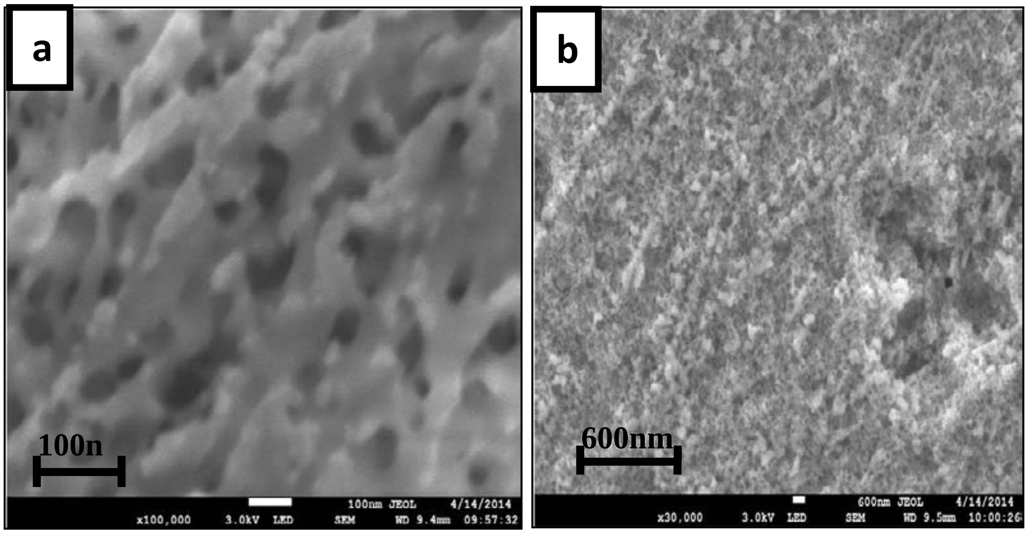
The equation (1) was used also to prepare the testing concentration. The resulted Raman spectra were measured by using the (Renishow Raman scope 2000) using (532nm) line of Ar^+-ion laser for excitation.

Results and discussion

surface morphology of (as-prepared) nano porous silicon

The morphological aspects of the nano (PSi) 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.

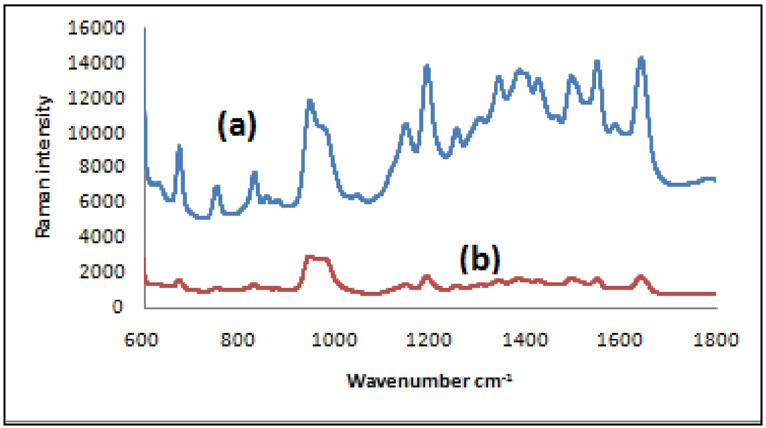
Figure(2a,b); show the surface morphology of (100) orientation nano (PSi) surface under etching times (5min). These nano (PSi) samples were prepared under (16 mA/cm^2) etching current density, (24%) HF acid concentration with illumination of blue laser diode(405 nm wavelength) and and (40mW/cm^2) intensity. It was found that the resultant nano porous structure, as shown in figure(2 a,b), has a pore-like fine structure with different pores shapes and pore widths. Figure(2 a,b); shows the (FE-SEM) image (top-view) at two magnifications (100,000 and 30,000) to give the reader a general and clear view of layer as well as a detailed view of surface morphology. The top view of the surface reveals that the porous layer is composed of a dense small pores aligned in random direction, with a diameter in the range(15 nm to 85 nm).



Figure(2): FESEM images showing (top view) of as-prepared nano porous surface prepared under etching conditions of 16 mA /cm^2 for 5 min etching time in (1:1) HF: ethanol solution with 405 nm ,40mW/ cm^2 laser illumination conditions for n-type(100) with different magnifications (a) 100,000 (b) 30,000.

Effecting the dipping time on activity of porous silicon/ Ag nanostructures

The activity of the (SERS) substrate for the detection of wide variety of molecules. This activity is depended on the enhancement process of the Raman signal which take place after the silver deposition process. In an attempt to achieve this goal, we examined several (PSi) samples and Ag^+ coated porous samples for their SERS activity, using s a crystal violet(cv) dye ($C_{16}H_{11}N_3O.HClO_4$). Figure (4) shows the direct comparison of SERS spectra of dye molecule for different dipping time (10 and 20) min in (10^{-2} M) $AgNO_3$ solution.



Figure(4) Raman spectra of 10^{-4}M crystal violet of (100) n-type PSi/Ag sample with silver nanoparticles deposited from 10^{-2} M $AgNO_3$ solution depending on deposition time (a) 10 min (b) 20 min. etching parameter J=16 mA/ cm^2, t=10 min.

The (SERS) show a peak value at a wave number of (950,1150,1550) cm^{-1} this value is a good agreement with that obtained by the researcher **(LEILA ZEIRI*etal*)** [13].

The main contribution to the SERS effect arises from an enhancement of local electromagnetic field dose to the metallic surface after localized surface Plasmon (LSP) excitation. The (LSP) coupling is affected by a deposition time of porous silicon in $AgNO_3$ solution. The maximum enhancement in SERS signal is observed at deposition time of 10 min this means that in order to form stable, well developed nanostructures and achieve optimal sizes of nanoparticles immersion for about (10min) is required. The increase of deposition time will led to form larger and more complicated nanostructures like nanoclusters which provide strong (SERS) signal and also the spectral reflectance of porous/ Ag substrate will increase and hence decrease the (LSP) coupling process.

The Effect of Dipping Time on Porous Layer

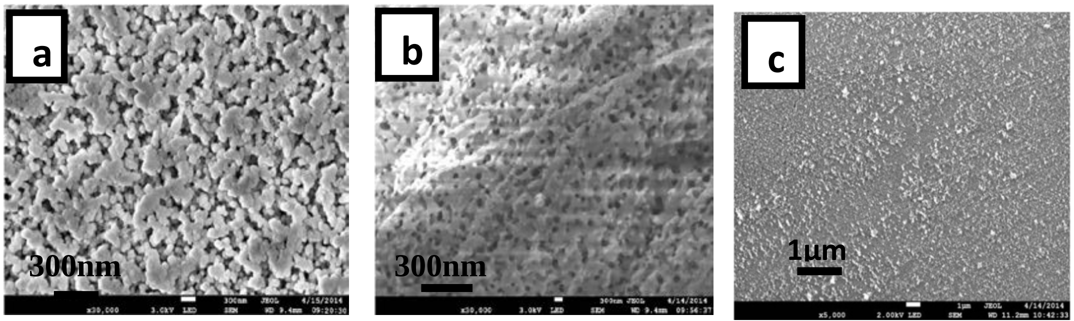
The effects of silver dipping time on the porous samples has been studied at different dipping times (10 ,15 and 20) min in (10^{-2}M) solution. The effect on silver dipping time on the morphology of deposited layer was examined by using FE-SEM images at different dipping time. Figure(3a,b,c), shows the FE-SEM image(top-view) of silvered nano (PSi) (100) n-type of etching time of (10 min) , as shown from this figure that the increase of the silver dipping time lead to form a uniform silver layer on the porous surface and uniformly distributed particles can be obtained with increasing the dipping time.

As shown figure(3 a) shows that only a partial coverage of the surface (80%) was obtained and the size of silver nanoparticle is in the range from (60nm to 100 nm) and these size was increased when two particles or more become closer to each other. The morphology and size of silver particles on the porous surface depends on the concentration Ag^+ in the deposition solution and on the duration of the process. The porous surface effects the initial nucleation site distribution. As the silver deposition process continues, the size of the silver particles increase due to coalescence of smaller nano size particles.

The Ag^+ reduction was carried out by the (PSi) layer and the process continues until the silver layer covered the overall porous surface. figure(3b,c) reflect a more uniformity the silver film above the nano porous layer and the silver island become bigger reaching to several nanometers. Thus, increasing the deposition time leads to the formation of a highly uniform layer, composed of layer silver particle in sub-micron level.

Therefore, from the above results we can reach to the following facts:

1- SERS –active substrates can be prepared for the relatively short period of time.
2- The process of the silver deposition can be easily controlled.
3- The optimum of silver deposition on PSi is about 10 min for partially covering the porous layer.

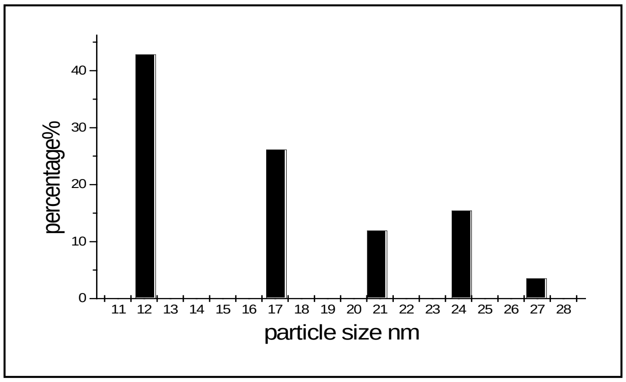


Figure(3): FESEM images of silver layer deposited on porous silicon from 10^{-2} M $AgNO_3$ solution at different dipping times (a)10 min (b)15 min (c) 20 min for n-type etching time of porosity 70% (active substrate).

Correlation Between SERS-activity of (PSi) Substrate and Morphological Parameters

Due to the dense arrangement of silver crystals, large local electric field concentrates in gaps between silver nanoparticles, resulting in strong enhancement of Raman signal. The silver crystallites cover porous sample does not affect it properties noticeably. Probably, only hydride-reducing bonds on silicon surface, which lie in the upper (outer) part of pores and between the pores, play a role for such film formation, resulting in higher enhancement of Raman signal with that of [14,15], there reach to the fact that the strongest field enhancement occurs exactly between sharp faces of closely positioned metal particle. figure(5) show the statistical distribution of pore size based on the porosity of the sample.

For the (70%) porosity the silver nanoparticle is the rang (12-27)nm with peak distribution silver nanoparticle at (12nm). The SERS signal show a significant peak at (950,1150,1550) cm^{-1}. thus we can calculated that the high SERS signal may due to the nano size at peak of (12 nm). This means that a good detection can be obtained with silver nanoparticle at peak value of (12 nm).



Figure(5):shows the statistical distribution of silver nanoparticle deposited on(100) n-type of porosity 70% at dipping time 10 min.

Conclusion

Nano porous silicon layer prepared by photo-chemical etching with short laser wavelength can be used to prepare porous silicon active substrate (Ag/Si-NPA) at (10min) dipping time in $AgNO_3$ solution. This active substrate was used to detect low concentrated (10^{-4}M) crystal violet through enhancing Raman signal. The signal shows a significant peaks at (950,1150,1550) cm^{-1}. The improvement in SERS signal can be employed to detect the chemical complex components material like crystal violet.

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