Laser synthesis of Si nanopillars-based SERS for efficient chlorpyrifos detection

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Abstract. A uniform and high-density Si nanopillars-based SERS layer was synthesized; as an efficient means, for detecting ultra-low concentration of chlorpyrifos. A low (20 %) laser pulse duty cycle of 405 nm wavelength and 600mW/cm² intensity from a laser diode was used to achieve laser–induced etching. A simple, low-cost, and stable current wave driver circuit was utilized to drive the laser diode. Structural and spectroscopic features of the based SERS layer and AuNPs/Si nano-pillars sensor were studied by scanning probe microscopy, (FESEM) images, x-ray diffraction patterns and Raman spectroscopy. The results revealed that the Si nano-pillars layer provided superior features for creating high density hot spot gaps. A uniform, high population and unique size distributions of (AuNPs) layers on the AuNPs/ Si nano-pillars layer were achieved by ion reduction process. The sensor performance displays an excellent detection of chlorpyrifos with an exponential relationship with Raman signal. The highest chlorpyrifos enhancement factor (EF= 1.1*10⁶) with minimum limit of detection (LOD= 22*10⁻⁸ M); equivalent to 0.07 mg/Kg, was obtained with Si nano pillars of high value altitude populated with partially three dimensions AuNPs layer. This limit of detection is much lower than the recognized (0.1 mg/kg) value by the European Union.

Keywords. Pesticides, laser duty cycle, nano pillar, hot spot regions, SERS.

1. Introduction

The chlorpyrifos is an insecticide with a powerful contact and toxicity. It has been widely used in the cultivation of vegetables, fruits and other crops [1]. The use of pesticides for killing pests always leaves some remains on the crops surface [2]. Gas chromatography [3], high-performance liquid chromatography [4] and thin-layer chromatography [5] are some methods adopted to detect the pesticides residual on the fruits surface. In recent years, Raman spectroscopy was considered as a benefit technique for analytical to valuate food safety and quality [6]. An emerging field in pesticides detection “Plasmonics” can examine the light and metallic nanostructures interaction at the interface of metal-dielectric [7]. Surface-enhanced
Raman scattering (SERS) is a powerful technique for analytical that have been use Plasmonics nanoparticles to get detailed pesticides molecules chemical information attached or adsorbed to the nanostructured metallic surface [8, 9]. A high peak SERS is required to detect pesticides at ultra-low concentrations [10]. Sizes and density of hot spots are the main factors related to the Raman signal intensity [11]. Si nano-pillars can work as an efficient template to form Plasmonics gold nanoparticles (AuNPs) of AuNPs/ Si nano-pillars SERS sensor; due to its superior topographical (density of nucleation sites) properties [12, 13]. The density of hot spots among Plasmonics nanoparticles and hence; the enhancement factor (EF) and sensitivity of AuNPs/ Si nano-pillars SERS sensor varies with the Si nano-pillars topography and it rises with the nucleation sites within the Si nano-pillars layer [8, 14]. The dependence of SERS sensor on the nano-pillars layer properties inspires the suitable driving circuit design to control the topographical properties. In laser–induced etching, the ability to pulsate a CW laser diode at low duty-cycles is very useful for controlling the Si nano-pillars. A laser in pulses mode can adjust the temperature rise of the Si nano-pillars layer during the etching [15]. Melting; and therefore destroying the Si nano-pillars due to heat accumulation within its low thermal conductivity layer is very significant when laser etching takes place at high intensities [16]. For this reason, laser operation with relatively low duty cycle, can minimize the heat accumulation and increase of the density of silicon Nano crystallites within the prepared layer [14]. In the current work, a uniform synthesis of high-density Si nano-pillars - based SERS layer is considered in order to obtain an efficient AuNPs/ Si nano-pillars SERS hot spots sensor for detecting ultra-low chlorpyrifos concentration. For this purpose, high-power diode laser at low duty cycle was adopted as an efficient pulsed laser–induced etching.

2. EXPERIMENTAL DETIALS

2.1 Laser diode driver circuit

Moderate power, NV4V41SF (600 mW-CW), (400 to 405 nm) peak wavelength and (0 to +30°C) operating temperature diode laser; supplied by (RENESAS Company U.S.A) was employed for pulsed laser–induced etching. The electro-optical characteristics at (25°C) temperature are presented in table 1. A simple, low-cost, stable current wave form, variable repetition rate and duty cycle operation driver circuit was built to drive this laser diode as illustrated in Fig (1). The circuit is a multifunctional vibrator with variable operating frequency and cycles. The duty cycle (n) and the frequency (f) depend on resistors P1 and P2, and the driving current is controlled by the variable resistor R4 that is connected in series with the laser diode. As R4 increases, the driving current reaches a threshold value, and when it decreases, the driving current rises and so does the emitting optical power. The transistor (Tip 122) in the circuit acts as a switch which gets saturated at (5 Amp) current as the following equations [17].

\[
\begin{align*}
  n &= 1 = \frac{P2}{P1} \\
  f &= \frac{0.69}{((2\times P1+P2)+1 \times \text{Cl}) \times \text{Cl}} 
\end{align*}
\]
Figure 1. Block diagram of laser driver circuit.

Table 1. Electro optical characteristics of laser diode at TC = 25°C.

| Parameter            | Symbol | Conditions         | MAX.  |
|----------------------|--------|--------------------|-------|
| Threshold Current    | \(I_{th}\) | CW                 | 180mA |
| Operating Current    | \(I_{op}\) | CW, \(P_o = 600\text{ mW}\) | 600 mA |
| Operating Voltage    | \(V_{op}\) | CW, \(P_o = 600\text{ mW}\) | 4.6V  |
| Slope Efficiency     | \(\eta_d\) | CW, \(P_o = 600\text{ mW}\) | 1.7W/A|

2.2 Chemicals

The solution concentration \((10^{-3})\text{ M}\) was prepared by dissolving suitable weight of high purity (99.9%) Chloroauric acid (supplied from (CDH)-India) in double distilled water as explained in [18]. Chloropyrifos, O, and O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphonothioate were used to prepare Chloropyrifos solutions at \(25*10^{-4}, 12*10^{-7}, 6*10^{-6}\) and \(3*10^{-5}\text{ M}\) concentrations by using the following equation [18].

\[
M = \frac{W}{V} \text{ M Wt.} \tag{3}
\]

Where \(M\) (mol) is the concentration of pesticide, \(W\) (g) is the weight of the chloropyrifos, \(M\) Wt. (g/mol) is the molecular weight, and \(V\) is the volume of the solution dissolved.

2.3 Formation of Si Nano-pillars-based SERS samples

Si nano-pillars samples with specific topographical aspects (surface roughness, pillar altitudes and density dangling bonds (Si–H)) were synthesized by 20% duty cycle pulsed laser induced etching in order to attain high density and small sizes hot spot regions’ SERS sensors. Si nano-pillars samples were fabricated on (100) plane, 3-5 \(\Omega\text{ cm}\) resistivity n-type silicon substrates. The silicon substrates were immersed in 20%
diluted HF solution and fixed on a bench by two Teflon clamps. The laser beam was focused normally on the Silicon substrates, also the internal photo current passes from the non-illuminated lower Si surface to laser illuminated top surface through the electrolyte as exposed in figure (2).

![Figure 2. Experimental set-up of pulsed laser–induced etching process.]

### 2.4 Synthesis of AuNPs/ Si nano-pillars’ SERS hot spots pesticide sensors

The AuNPs/Si nano-pillars’ SERS hot spots pesticide sensors was fabricated at room temperature by gold-ion reduction process for 120sec. Once the Si nano-pillars sample is dipped in the HAuCl₄ solution, the Au nanoparticles start to form as a result of gold ion reduction via the (Si–H) nucleation sites. The density of these nucleation sites at the Si nano pillars is enormous; which helps materializing the Au nanoparticles growth. The Au ions reduction is explained in the following equations [19]:

\[
\text{Si} + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 4\text{H}^+ + 4\text{e} \quad (4)
\]

\[
\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au} \quad (5)
\]

The fabricated hot spots pesticide sensors were immersed into 25*10⁻⁸, 12*10⁻⁷, 6*10⁻⁶ and 3*10⁻⁵ M concentrations of Chlorpyrifos solutions for 5min and dried in air at room temperature before carrying out the SERS measurements.

### 2.5 Instrumentation

The structural properties of Si nano pillars and AuNPs/ Si nano-pillars SERS hot spots sensors were characterized by scanning probe microscopy (SPM) in contact mode; using 400 AFM system, (MIRA3 TESCAN) field–Emission scanning electron microscope FE-SEM and X-ray diffraction (XRD-6000, Shemadzue). The sizes of AuNPs and of the hotspot region were calculated by utilizing the program image
J2. Raman and SERS spectra which recorded by an APUS TESCAN Raman microscope using a continuous wave 532 nm wavelength DPSSND: YAG (10 mW) excitation laser.

3. Results and discussion

3.1 Characterization of Si Nano-pillars based SERS layer

The topographical properties of Si nano-pillars layer including (altitudes, shape and surface roughness) were studied by analyzing the 3 and 2-D micro AFM images. Figure (3a, b), showed the micro images of silicon nano pillars; formed in a distinguishable manner. It illustrates uniform and high-density Si nano-pillars over the Si surface. The profile depth of pillars has high degree of uniformity with an average altitude of about 54 nm. This represents high density of nucleation sites for the gold ion reduction process. This superior topography is attributed to the low tendency of heat accumulation within the Si nano pillars. Hence it decreases the Si dissolution process among pillars in the nanostructures layer, where; the Si nano-crystallite layer has much lower thermal conductivity than the bulk Si [20].

![Figure 3. (a) 3D AFM images of Si Nano-pillars -based SERS layer.](image1)

![Figure 3. (b) 2D AFM images of Si Nano-pillars -based SERS layer.](image2)

![Figure 3. (c) Histogram of Si Nano-pillars -based SERS layer.](image3)
The size histogram of Si Nano pillars illustrated in figure (3c). The average diameter, surface roughness and root mean square of these pillars sample were 58.18, 10.5 nm and 12.1 nm respectively. For these pillars, the PL spectrum is depicted in Fig. 4. The PL peak position is located at 600 nm; which represents the energy band gap of 2.06 eV. The PL spectrum of silicon nano-crystallites showed a dependency on the sizes of Si nano-pillars. This resulted showed an excellent agreement with the quantum confinement effect of charged carriers within the matrix of Si Nano-pillars [21]. The PL peak emission wavelength is related to the decreased dimensions of Si Nano pillars [22]; with an energy gap that depends on Nano pillar d(x) and d(y) and given by the following equation [23].

\[
E_{\text{g} (\text{ev})}^{\text{nano pillar}} = E_{\text{g} (\text{bulk Si})} + \frac{\hbar^2}{8} \left( \frac{1}{d(x)} + \frac{1}{d(y)} \right) \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right]
\]

(6)

Where; \(E_g = 1.12\) eV bulk Si energy gap, \(\hbar = 4.13 \times 10^{-15}\) eV Planck’s constant, \(m_e^* = 0.19m_0\), \(m_h^* = 0.16m_0\), and \(m_0 = 9.1 \times 10^{-31}\) kg.

3.2 Structural properties of AuNPs/Si nano-pillars SERS hot spots pesticides sensor

The morphological aspects of (AuNPs) deposited on Si nano-pillars presented in Figure 5a. The FE-SEM micro image of the deposited gold nanoparticles by ion reduction showed a distinguishable Au nanoparticles on the Si surface. They have spherical shape with significant aggregation tendency. This figure shows clearly the hot spots regions (vacancies) among the Au nanoparticles. The Si nano pillars act not only as a source of electrons for the Au ion reduction but it also defines shape, sizes, and spatial arrangement of the AuNPs. Nanopillars Si based SERS hot spots pesticides sensors are characterized by their highly ordered pillars regions which were vertically grown in the Si wafer. This indicated a better performance of the SERS signal [24].

**Figure 4.** PL spectrum of Si Nano-pillars-based SERS layer.
Figure 5. (a) FE-SEM micro image of AuNPs/Si Nano-pillars SERS hot spots pesticides sensor.

Figure 5. (b) histogram of AuNPs size of AuNPs/Si Nano-pillars SERS hot spots pesticides sensor.

Figure 5. (c) Hot spot regions of AuNPs/Si Nano-pillars SERS hot spots pesticides sensor.

The histogram of AuNPs size and hot spot regions is illustrated in 5a and b respectively. The AuNPs size were in the range (5 to 65) nm, and the hot spot region were in the range (5 to 55) nm with the peaks of
both histograms are located at 25 nm. The topographical feature of AuNPs/ Si nano-pillars layer is shown in Fig. (6a) and (6b) which represent 2D and 3D AFM images of the layer after depositing gold nanoparticles. This figure showed clearly a reduction of both the average Si nano pillars’ altitude from 54 nm to about 26nm, and the root mean square surface roughness from 12.1nm to about 7.9nm. The average Si nano pillars’ diameter, however, increased from 58.18nm to 83.7nm. These results refer to a deposition of AuNPs in x and y- direction, which consequently reduce the depth and surface roughness and increase the width of the Si nano pillars in the z –direction (metallic decoration). These results can also mean a finger prints consideration of the AuNPs sizes location of dangling bonds (nucleation sites) within the Si nano pillars features. In reference to the average Si nano pillars’ diameter, at the high energy sites the higher nucleation is contained; as in the region of sharp nano pillars [25].

Fig. 7 shows the EDX analysis of AuNPs/ Si nano-pillars SERS hot spots sensor. The results confirm the existence of AuNPs on the Si nano pillars. This figure proves the growth of high density of AuNPs with the Si alone existence, without any additional elements.

![Figure 7. EDX analysis of AuNPs/ Si nano pillars SERS hot spots pesticides sensor.](image)

| Elements | Weight % |
|----------|----------|
| Si       | 13.2     |
| Au       | 86.8     |

The XRD pattern of AuNPs/ Si nano-pillars SERS hot spots pesticides sensor presented in figure 8. The Si nano pillars were still crystalline along the 100 direction at 2θ (33.5°) angle of diffraction. The XRD of AuNPs demonstrated reflections of specific Bragg’s at 2θ diffraction angles of about 38.2° and 44.3° for the planes 111 and 200 respectively. The exclusive nanostructured parameters of integrated AuNPs (grain size (D) is calculated from Scherer equation [26] and the specific surface area (S.S.A.) is calculated by the equation [27].

\[
S.S.A = \frac{600c}{\beta \cdot \rho}
\]  

(7)

Where; ρ (19.3 g / cm³) is the density of AuNPs. The grain size of AuNPs is about (3.6 nm) in the (111) plane, therefore, the value of S.S.A is about 86.02 m²/g.
3.3 Detection performance of AuNPs/Si nano-pillars SERS hot spots pesticides sensor

The Si nano pillars were initially examined at higher concentration (10^{-2} M) of Chlorpyrifos solution. Very weak Raman response was noticed, as shown in figure (9). The Raman peak improved dramatically after incorporating the AuNPs on Si nano pillars, due to the SERS effect. The prepared AuNPs/ Si nano-pillars SERS hot spots pesticides sensors were experimented with Chlorpyrifos solutions at 25*10^{-8}, 12*10^{-7}, 6*10^{-6} and 3*10^{-5} M concentrations, as shown in figure (9). The significant Raman peaks in the SERS chlorpyrifos spectrum are related to P-O stretching, C-C stretching, C-Cl stretching, P=S stretching, and P-O-R stretching bonds at 345 cm^{-1}, 536 cm^{-1}, 615 cm^{-1}, 677 cm^{-1}, and 1099 cm^{-1} respectively [28]. These Raman peaks are the fingerprint of chlorpyrifos pesticide.

To carry out a quantitative analysis of the fabricated pesticides sensors, a relationship between the characterized peak intensity 675 cm^{-1} of the SERS signal and the concentrations of chlorpyrifos was established as illustrated in Figure 10. This figure displays an exponential relationship between them at Chlorpyrifos concentration of 25*10^{-8} to 3*10^{-5} M. This relationship provides ultra-high Raman signals. The results have been obtained clarified the possibility of those Si nano pillars for the Chlorpyrifos analysis in its solutions. The main reason behind this performance is connected to the hot spot regions density among the AuNPs, as well as to the S.S.A of the Au-NPs itself. An energy transfer efficient between the AuNPs and the pesticide molecules inside the regions of hot spot can improve the detection efficiency of the sensors towards the pesticide and hence; enhances the Raman signal. The most important parameter for assessing the activity of the present sensors, in addition to their linearity, is the enhancement factor (EF) that is determined using the equation (8) [29].

The enhancement factor (EF) of the Raman peak intensity was determined by the Raman peak targeting of the Chlorpyrifos molecules, using to the following equation:

\[
EF = \frac{I_{SERS} \times C_R}{I_R \times C_{SERS}}
\]  

(8)

Where; \(I_{SERS}\) and \(I_R\) represent the counterpart SERS intensities and normal Raman, while \(C_{SERS}\) and \(C_R\) are SERS and normal Raman concentrations of the Chlorpyrifos molecule respectively.
Figure 9. SERS spectra of chlorpyrifos with different concentrations from $25\times10^{-8}$ to $3\times10^{-5}$ M for AuNPs/Si nano-pillars SERS hot spots pesticides sensor.

Figure 10. An exponential correlation between SERS intensity against Chlorpyrifos concentration at highest peak of 675 cm$^{-1}$ for AuNPs/ Si nano-pillars SERS hot spots pesticides sensor.

Figure (11) presents the EF versus the concentrations of chlorpyrifos pesticides solution. This figure signifies the stable sensor performance without any saturation effects. This means a continuous rise of the EF with the decreasing concentration of pesticide. Ultra-low molecules concentrations increase the probability of a target molecule to be located in the region of hot spot; leading to its detection and an increase in the EF by strengthen the SERS signal. The highest EF of chlorpyrifos ($1.1\times10^6$) was obtained at ultralow ($25\times10^{-8}$ mol./L) concentration. This high value of the EF has resulted to comprise the surface of AuNPs/ Si nano-pillars SERS hot spots sensor on an enormous hot spot regions density terribly needed by the reaction [30].

The LOD of AuNPs/Si nano-pillars SERS hotspots pesticides sensor for chlorpyrifos was calculated using equation (9). The limit of detection (0.07 mg/Kg) was obtained with 20% duty cycle at $25\times10^{-8}$ M concentration. The obtained LOD limit is much lower than what’d been published in recent studies. Zhai et al. [28] reported that the chlorpyrifos detection limit have been estimated to be 0.13 mg/kg, which is smaller than the result of Liu et al [31]. The limit of detection (LOD) was determined in accordance with the dependency on the feature of the SERS peak, using the following equation [28]:

$$\text{LOD} = \frac{3S_d}{d}$$  \hspace{1cm} (9)

Where; $S_d$ is the SERS intensity standard deviation for blank samples at Raman shift, and d refers to the plotted calibration curve slope.
Conclusions

In the present work, very sensitive, and low cost and effective AuNPs/ Si nano-pillars SERS hot spots pesticides sensors were synthesized on uniform and high-density silicon nano pillars as an efficient based SERS layer for detecting ultra-low chlorpyrifos concentrations. Low laser pulse duty cycle of short wavelength diode laser and high intensity pulsed laser–induced etching were employed to achieve our goal. The highest EF and minimum limit of detection were obtained with Si nano pillars of high altitude which partially populated with three dimensions AuNPs layer. All present findings are within the context of the published work. This work is fully supported by the theories and the results are genuine and contribute further to the field of pesticides detections; especially those at trace levels.

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