Synthesis and characterization of porous silicon gas sensors

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Abstract. In this work, photo-electrochemical etching process of n-type Silicon of resistivity(10 Ω.cm) and (100) orientation , using two illumination sources IR and violet wavelength in HF acid have been used to produce PSi gas detection device. The fabrication process was carried out at a fixed etching current density of 25mA/cm² and at different etching time (5, 10, 15 and 20) min and (8, 16, 24, and 30) min. Two configurations of gas sensor configuration planer and sandwich have been made and investigated. The morphological properties have been studied using SEM, the FTIR measurement show that the (Si-Hx) and (Si-O-Si) absorption peak were increases with increasing etching time, and Photoluminescence properties of PSi layer show decrease in the peak of PL peak toward the violet shift. The gas detection process is made on the CO₂ gas at different operating temperature and fixed gas concentration. In the planner structure, the gas sensing was measured through, the change in the resistance readout as a function to the exposure time, while for sandwich structure J-V characteristic have been made to determine the sensitivity.

1. Introduction
PSi is one of the most important substance because of its perfect morphological, electrical, and mechanical characteristic [¹]. The high surface area to volume ratio is about (500-1000m²/cm³) of PSi, the ease of manufacturing, several morphology can be obtain for different preparation condition result in the formation very promising material for developing a smart systems-on-chip sensors. Several modern gas sensing systems are has been developed as a means for comparing both the performance and the physical sensing gas sensor is defined as any device that assesses one or more characteristics of a sample of gas [²]. The Photo-electrochemical Etching (PECE) is a combined between the electrochemical etching process and photochemical etching where light or laser illuminating on the silicon electrode during the anodization process can be utilized to modify the micro porous and macro porous properties. Where At the top layer due to light absorption, which leads to further reduction in size the number of nano-crystallites and PSi layer thickness were affected by illumination wavelength [³]. The following equation shows the overall reactions for the pore formation. The following equation shows the overall reactions for the pore formation [⁴]:

\[
\text{Si} + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}^+ + 2e^-
\]

(1)
There are two specific configuration of sensing mechanism Planar and Sandwich structure. In the first one the electrical current will pass in the porous layer only while in the second mechanism the current will flow cross the porous layer and formed silicon heterojunction between PSi and Si the sensing process will vary based on the current flow in the porous layer and the PSi/Si junction. It is important to use porous silicon instead of silicon in the gas sensor application this is due to the increasing in responsively, ease of manufacturing by etching process which is simple and cheap, also it can be produced with different morphology, and can use several techniques to obtain the readout[5].

2. Basic Gas Sensing Characteristics
The main parameter of the gas sensor including the gas responsivity(R), gas concentration, sensing limit of gas detection, response(τ_res) and recovery time(τ_rec), and the detection temperature [6]. These parameters are varied based on the porous silicon parameter especially the pore size, porosity, and surface to the volume ratio.

2.1 Response time and recovery time
One of the most important parameter of the gas sensor device is the response time (τ_res) which can be defined as the exploited time for the gas sensor device to make dramatic change in the physical parameter from the beginning of the reaction until getting to a stable readout when it reached spatial percentage scale (generally take as 95%) of the last value, in response to the changing in the input [7]. The reduction in the response time is a good properties for gas detection device. With high gas concentration, the response time is short. So in the case of operation with low concentration of the toxic gases must be careful because long response time would be dangerous. The response time for typical gas sensor is in the order of a few minute or lower than that [8].

2.2 Selectivity
Generally the selectivity of the gas sensor device is defined as the capacity of sensor to characterize a given gas concentration with the presence of other gases at the same sensing condition [9]. For example the O₂ sensing device dose not response to another gases like CO, NO and NH₃, so this device considered as a selective device. The selectivity of nano material based gas sensor device is given by the following equation [10].

\[
\text{Si} + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2)
\]

2.3 Detection Limit
The detection limit is defined as the minimum magnitude of the calculated that can be determine by the sensor, on the other word is the lower value of gas concentration that can be sensed by gas detection device. The sensing device performance enhanced with decreasing the detection limit [11].

2.4 Gas response (sensitivity)
The gas responsivity for gas detection device can be define as the dramatically change in the resistance or other physical quantities of the sensor surface before and after exposure to gas. The researchers have used different mathematical terms to define the gas response as shown in the following equations [12].

\[
R = \frac{R_a - R_B}{R_a} \times 100 = \frac{\Delta R}{R_a} \times 100\% \quad (3)
\]
\[ R = \frac{I_a - I_g}{I_g} \times 100 \% \]  

(4)

Where Ra is the resistance of the sensor in the presence of atmospheric air, while Rg the device resistance after exposure to the gas, Ia the essential current of PSI sensor in the presence of atmospheric air, and Ig is the current after exposure to gas. The sensitivity is the capability to sense a lower concentrations of using gas [13]. Sensitivity characterizes the magnitude of a response to a particular analyse [14]. The sensitivity can be recorded as a ratio between some measure of the response and the concentration of analyse being delivered.

3. Experimental part

A commercially available Si wafer (100) n-type of resistivity (10Ω.cm) and thickness (625µm) were used. The experimental setup consisted of power supply, ammeter and aqueous (HF) acid in Teflon cell with ethanol to prevent the aggregation of H₂ bubbles, and laser. The PSI formation condition including for IR (810nm) and intensity (2W/cm²) the etching times 5, 10, 15, and 20 min, the HF concentration of about 24%. While for violet (405nm) and intensity (20mw/cm²) the HF concentration of about 16% and fixed current density 25mA/cm². Also there were two electrodes, the Si wafer connected to the anode and platinum used as the cathode. The PSI silicon sample were prepared by PECE process with constant current density (25mA/cm²) for both lasers, and at different etching time of about 5 to 20 min for IR illuminated PSI samples and 8 to 30 min for violet illuminated samples and the etching solution consisted of HF : ethanol : H₂O (1:1:1), and the HF concentration was (16%). Experimental setup is shown in Figure 1.

![Figure 1. The schematic of PECE.](image)

After the formation process the gas sensor application required deposition of AL electrode. Two configuration of electrode have been done for planer structure of gas sensor grid mask with thickness 250nm on the PSI surface have been formed and for sandwich structure the electrode made on the upper PSI surface with thickness (5-20nm) and lower PSI surface with AL electrode, as shown in the following Figure 2. This deposition was done by using the vacuum thermal evaporation.

![Figure 2. PSI sample (a) planer (b) sandwich](image)
4. Result and discussion

4.1 Characteristic of porous silicon layer

One of the most important structural properties of PSi material is the formation pores (or porosity %), the PSi preparation parameter including (HF) concentration, laser properties such as (wavelength, illumination intensity), and the percentage of the doping in the Si wafer. All these parameters monitoring the nanosize of the pore, how the channel distributed, the channel connectivity. The most common structure of the PSi preparation are circular pores with ‘branching’ through the surface. Also it can be noted that the nanosize of the high thickness porous silicon reduced with the depth of layer. The porosity % (P %) and layer thickness of PSi (d) can be calculated gravitationally by the following equations[15].

\[ P = \frac{(M_1-M_2)}{(M_1-M_3)} \]  
\[ d = \frac{(M_1-M_3)}{\rho \times A_{PSi}} \]

Where \( M_1 \), the PSi sample mass before anodization process, \( M_2 \), the PSi sample mass after anodization process, and \( M_3 \), the sample mass after removing the PSi layer using NaOH electrolyte, \( \rho \), the Si bulk density and its unit is (g/cm\(^3\)), and \( A_{PSi} \), the PSi area in (cm\(^2\)).

Figure 3. The porosity of the porous silicon as a function to the etching time for two illumination wave length (a) IR (810nm), (b) and violet (405nm).

'Figure 3a' shows the case of IR, after certain time the porosity increased linearly and reaching to high value of about 83%. The increasing of etching time to higher value of 20min, the PSi layer became fragile with low mechanical properties. For case of violet illumination of 'figure b', the porosity increased with increasing the etching time in an exponentially relationship, and the maximum value was about 88% at 30min etching time. The higher etching time allowed deeper penetration through silicon region and produced more pore, and this results was comparable with the results obtain by other researchers[16]. The relationship between the layer thickness and the etching time shown in the Figure 4. In this Figure the value of the PSi thickness layer increased with increasing etching time. The higher value of the layer thickness was about (38.43\( \mu \)m) and (23.8\( \mu \)m) for IR and violet illumination respectively.

Figure 4. The layer thickness of the porous silicon as a function to the etching time for two illumination wave length (a) IR (810nm), (b) and violet (405nm).
The layer thickness of IR was much greater than that of violet illumination. This was due to the increasing of the absorption depth for (810nm), where the absorption depth was about (12.9μm) while for violet (405nm) it was about (100nm). Long laser wavelength increases the penetration depth of incident photons and the etching would occur at region away from the porous layer and inside the deep silicon regions so much greater e-h pairs would be generated and this would increasing the silicon dissolution process. The morphological properties of porous layer like, pore shape, pore width, and the wall thickness between the adjacent pores are strongly depended on the etching parameters especially the etching time, current density, and the laser illumination conditions (intensity and wavelength) [17, 18]. These properties of (PSi) have been investigated by direct imaging for the structure by using Scanning Electron Microscope (SEM).

Figure (5). SEM image (top-view) of IR illuminated porous layer, 2W/cm² illumination intensity (a)5, (b)10, (c)15, and (d)20 min with 6200 magnification for (a, b and c) and with 1600 magnification for d.

The increasing of the etching time would improve the silicon dissolution mechanism due to increases the amount of the photo generated e-h pairs and hence the pore size and the pores overlapping process leading to synthesis the rectangular form (pores). From this images, some basic observations may be taken into account based on the ;(i) Pore size of the porous layer seems as a macro pores with different pore shapes nearly spherical and rectangular forms ;(ii) The pores was randomly distributed on the silicon surface, the large value of the pore sizes may be attributed to the increase of e-h pairs within the porous layer, which enhanced the silicon dissolution process between the nearest-neighbor pores. The non-uniformity of Gaussian distribution of the laser beam intensity led to make the etching rate having different values and hence resulting a porous layer with different pore size. While for the PSi sample prepared with violet laser the formation of this rare morphology was studied by Cláudia [19], according to the analysis of removing the silicon atoms remains enhancing the surface in homogeneity due to the local changes in the electric field distribution. This type of morphology occurred at high value of applied voltage where (30V) DC was supplied across the silicon and Pt electrodes compared with (1.5-2V) in the case of IR illumination. By comparing the SEM images, we can observe that the increasing of the etching time would lead to increase the density of the cross-like pore structure. The growth rate of the pore across the PSi layer was not constant along the depth. This referred to the fact that etching occurs only in the pore tip but also in the pore walls. The high electric field at the pore corner maybe responsible for this behaviour, where high bias voltage led to so-called pore wall break down [19].
Figure 6. SEM image (top view) of violet illumination PSi layer prepared and (20mW/cm²) illumination intensity (a) 8, (b) 16, (c) 24, (d) 30 min with 3600 magnification for (a, b, and d) and 2700 magnification for (c).

4.2 Photoluminescence studies
Photoluminescence spectroscopy has emerged as an important tool for studying the optical properties of PSi materials suited for gas detection process. PL studies was carried out using He-Cd laser system operating at 325nm wavelength. The PL spectra of PSi prepared with different etching times under two illumination wavelength IR and violet as showing in the following figure respectively. The PL spectra of PSi were dominated by strong and broad emission peak spanning over a large part visible region. i.e PSi sample showed strong emission wavelength in the range (500-750nm). The emission was attributed to the radiation carrier recombination process in the silicon nano region. The PL intensity increased with increases the etching time with blue shift in the peak position.

Figure (7). Illustrates the PL spectra of IR PSi sample at different etching times, (a) 5 min (b) 10 min, (c) 15 min, and (d) 20 min.

While ‘Figure 8’, displays the PL spectra of sample prepared with violet laser the increasing of the etching time showed a strong emission at different wavelengths 655, 605, 573, and 535 nm respectively, with a blue shift in the peak position.
Figure 8. Illustrates the PL spectra of violet PSi sample at different etching times, (a) 8min, (b) 16min, (c) 24 min, and (d)30 min. By comparing the PL spectra of Figure 7 and 8, it can be recognized that the PL spectra of violet illumination, the PL intensity with short emission wavelength has high value. While for the samples prepared by an 810 nm, there was low PL intensity and this would be as a result of bigger nanocrystalline size due to its small photon energy (1.53eV), which was not sufficient enough to initiate the absorption and reduce the silicon nano size. To PL contribution limit so the increasing of the illumination wavelength (decreasing the photon energy) led to synthesis larger silicon nano size. When the silicon sample illuminated with short wavelength (405nm), the photon energy was (3.062eV). The average of the silicon nano crystallite, energy gap of the porous layer, the peak of PL intensity and emission which determine from the above figures and according to the following equation [20] are showed in Table 1.

\[
E_{g(PS)} = \frac{hc}{\lambda_{max}} \quad (7)
\]

\[
E_{g(PS)} = E_{g(S)} + 88.34/L^{1.37} \quad (8)
\]

Where h is blank constant, c is the light speed , and \( \lambda_{max} \) is obtain from the PL curve and then can determine the nano size L.

### Table 1. Illustrates, PL emission wavelength, PL intensity, energy band gap, and silicon nano size as a function to the etching time for two illumination wavelength IR and violet

| Illumination Source | Etching time (min) | PL peak Wavelength (nm) | PL intensity (a.u) | \( E_g \) (eV) | Nano silicon size (nm) |
|---------------------|-------------------|-------------------------|-------------------|--------------|----------------------|
| IR                  | 5                 | 752                     | 1200              | 1.7          | 3.9                  |
|                     | 10                | 720                     | 1335              | 1.72         | 3.8                  |
|                     | 15                | 688                     | 1466              | 1.8          | 3.4                  |
|                     | 20                | 675                     | 1250              | 1.84         | 3.3                  |
| Violet              | 8                 | 690                     | 1705              | 1.82         | 3.4                  |
|                     | 16                | 630                     | 1780              | 1.97         | 2.9                  |
|                     | 24                | 600                     | 1930              | 2.06         | 2.75                 |
|                     | 30                | 250                     | 2100              | 2.24         | 2.72                 |

4.3 Gas sensor properties
The gas sensing performance of two types of porous silicon configuration (planer and sandwich structure) were studied at different operation temperatures.
4.3.1 Sandwich structure mode

Sensing mechanism of this mode of operation was based on the response of the current density -voltage characteristic across the porous silicon /crystalline silicon junction.

4.3.1.1 Current density –voltage characteristic of sensor without gas

'Figure 9a', 'Figure 9b', 'Figure 9c' and 'Figure 9d' present the J-V characteristics of IR illuminated sandwich (Al/nPSi/n-Si/Al) structure at different temperatures from (25-150°C). All measurements were taken in the range from (0 – 5V).

Figure 9. J-V characteristic for IR illuminated porous samples at the different temperatures (a)25°C, (b)50°C, (c)100°C, (d) and 150°C for different etching times(5,10,15,and 20 min).

Figure 10. J-V characteristic for violet illuminated porous sample at the different temperature (a)25°C, (b)50°C, (c)100°C, (d) and 150°C for different etching times(8,16,24, and 30 min).

From these curves, we can observe that the current passing in the absence of gas molecule was varied according to the porosity and the layer thickness of the porous layer. The following facts can be conclude.

1- At fixed temperature the forward current passing through the fabricated sandwich structures deceased with increasing the etching times for both types of illuminated porous silicon samples. This behavior was due to the increasing the porosity and layer thickness with increasing the etching time, where the increasing of the porosity led to decrease both of the dielectric constant of the porous silicon layer and the mobility of the charge carrier.

2- At fixed etching time the value of the forward current increased slightly with increasing the operation temperatures from 25°C to 150°C due to the increase of the thermal generated charge carrier with temperature.
In prepared device, the forward current density –voltage (J-V) behavior followed a power law relationship (J α V^2) which indicated the space charge current attributed to the carriers drifting through the high resistivity luminescence Psi. According to the suggested model by Pang, C et al [21] for the carrier transport in PSi photoluminescence device was rectifying. In forward bias, the (J-V) characteristics exhibits a power-law relationship (J=kv^m) where k was proportionality factor depending on the characteristics of the porous layer and m=2 which implied that the total current of the device was dominated by carrier transport in the high resistivity luminescence. The device can be modeled as an intrinsic semiconductor luminescence sandwich between two conduction material Aluminum electrode and the n-type silicon substrate. The intrinsic semiconductor (PSi layer) contained a limited amount of thermally generated free carrier. In forward bias, electron and hole were injected into PSi layer .When the injected carrier concentration became comparable to the thermally generated concentration, the J-V characteristics of the device deviated from ohmic behavior according to the equation.

$$I_{psi} = \epsilon_{psi} \epsilon_0 \mu_{eff} V^2/d^2$$  \hspace{1cm} (9)

Under the pressure of about (5%) ppm CO2 the current density –voltage characteristic with gas. For both curves, exposure to CO2 gas did not change the shape of J-V characteristic (still rectifying) but the values of the current at presence of CO2 gas were higher than that of the case without gas, the variation in the current indicating that the sensor was very sensitive to CO2 gas. The variation of the current at maximum applied voltage ±5V at fixed operation temperature before and after exposure to CO2 gas increased with increasing the etching time. The structure of (Al/nPSi/n-Si/Al) with violet illuminated samples has higher variation in current compared with structure of (Al/nPSi/n-Si/Al) with IR illuminated samples. The increasing of the current density for all samples related to the role of the CO2 molecules where desorption of the molecule on the PSi layer was due to the Vander Waals interaction which would lead to modify the dielectric constant of the porous layer, whereas we see in the presence of the CO2 gas would enhance the current flow in the fabricated sensor. According to the CO2 molecules that acted as acceptor, this would lead to an increasing the free carrier concentration [14].

![Figure 11](image1.jpg)

**Figure 11.** Illustrated the J-V characteristics for IR illuminated porous sample at different temperatures (a)25 °C, (b)50°C, (c)100 °C, (d) and150°C under CO2 gas at pressure of about (5%)ppm.

![Figure 12](image2.jpg)

**Figure 12.** Illustrated the J-V characteristics for violet illuminated porous sample at different temperatures (a)25 , (b)50°C, (c)100, (d)150°C under CO2 gas at pressure of about (5%)ppm.
The variation of the maximum detection sensitivity at fixed operating voltage 5V with operating temperature in the range from room temperature to 150°C of the porous layer shown in the figure (13). The sensing test was performed using (5%ppm) CO₂. Temperature variations revealed the current passing through the sensor, so the sensitivity of the device increased with raising in the operating temperature from 50°C to 150°C and reached a maximum at 150°C. Also by comparing figure (a) and (b) it clear to us that the violet illuminated sample have higher sensitivity than the IR illuminated sample. This is due to the fact that the increasing of the effective dielectric constant of the porous layer under CO₂ exposure. This may be attributed to the rate of the adsorption of the CO₂ gas molecules on active porous layer increased with rising in the operating temperature. This causes a rapid increasing in the passing charge carriers and hence an increasing in the sensitivity as shown in Figure 13.

![Figure 13. The variation of the sensitivity at 5V applied voltage for porous sample with operating temperatures (a) IR illuminated PSi (b) violet illuminated PSi.](image)

4.3.2 Planer structure mode
The sensing mechanism of this type of sensors operation was based on the recording the variation of the resistance of the porous layer. Parallel strip electrodes with two opposite E latter were used for measuring the electrical resistance of PSi device. The resistance was measured at different temperature and fixed operating voltage of about 3V.

4.3.2.1 Dynamic response
Dynamic response of the planer structure gas sensor at fixed concentration of using gases for two type of porous silicon substrates IR and violet illuminated PSi samples.

![Dynamic response](image)
Figure 14. Dynamic response of IR illuminated PSi sample planer structure sensor at different temperatures under CO2 concentration (5%)ppm at specific etching times (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min at current density (25mA/cm²) and fixed illumination intensity of about (2W/cm²).

Figure 15. Dynamic response of violet illuminated sample planer structure sensor at different temperatures under CO₂ concentration (5%)ppm at specific etching times (a) 8 min, (b) 16 min, (c) 24 min and (d) 30 min at current density (25mA/cm²) and fixed illumination intensity of about (20mW/cm²).

From the dynamic response curves, it’s easily to observe that a large resistance variation is recorded. The resistance of porous layer recovers slowly and tend to retain to the initial value for IR and violet illuminated samples at different temperature and specific etching time. The resistance of porous layer shows a decrease from higher value to lower value and the numerical value of the resistance is varied according to the etching time and the temperature. The resistance value, before and after exposure to CO₂ gas of PSi layer has been tabulated in the following table also the response and recovery time for all planer structure PSi sample sensor.
Table 2. Dynamic response for planer configuration porous with IR illuminated PSi layer.

| Etching time (min) | Temperature (°C) | Maximum resistance (MΩ) | Minimum resistance (MΩ) | Response time (sec) | Recover time (sec) | Maximum sensitivity |
|-------------------|------------------|--------------------------|--------------------------|--------------------|--------------------|---------------------|
| IR 5min           | 25               | 1.493                    | 1.435                    | 130                | 120                | 3.804796            |
|                   | 50               | 1.377                    | 1.327                    | 100                | 160                | 3.631082            |
|                   | 100              | 1.210                    | 1.143                    | 110                | 80                 | 5.371329            |
|                   | 150              | 1.092                    | 0.879                    | 80                 | 80                 | 10.33114            |
| 10min             | 5min             | 3.244                    | 1.60                     | 160                | 160                | 40.50555            |
|                   | 50               | 2.194                    | 1.472                    | 120                | 200                | 14                 |
|                   | 100              | 0.938                    | 0.751                    | 150                | 180                | 17.95045            |
|                   | 150              | 0.703                    | 0.259                    | 90                 | 100                | 21.07611            |
| 15min             | 25               | 4.78                      | 3.2                      | 125                | 170                | 33.05419            |
|                   | 50               | 2.520                    | 2.1                      | 150                | 140                | 16.05667            |
|                   | 100              | 1.920                    | 1.113                    | 150                | 200                | 22.53125            |
|                   | 150              | 0.915                    | 0.561                    | 165                | 210                | 38.68852            |
| 20min             | 25               | 12.2                      | 5.2                      | 30                 | 75                 | 62.23333            |
|                   | 50               | 10.960                    | 9.74                     | 155                | 180                | 16.57034            |
|                   | 100              | 8.820                    | 7.29                     | 140                | 200                | 13.42923            |
|                   | 150              | 5.560                    | 4.44                     | 170                | 150                | 19.2446             |

Table 3. Shows dynamic response for planer configuration porous sensor with violet illuminated PSi layer.

| Etching time (min) | Temperature (°C) | Maximum resistance (MΩ) | Minimum resistance (MΩ) | Response time (sec) | Recover time (sec) | Maximum Sensitivity |
|-------------------|------------------|--------------------------|--------------------------|--------------------|--------------------|---------------------|
| violet 5min       | 25               | 3.452                    | 2.88                     | 130                | 180                | 20.64               |
|                   | 50               | 1.990                    | 1.63                     | 140                | 113                | 18.0402             |
|                   | 100              | 1.352                    | 0.811                    | 50                 | 90                 | 54.80769            |
|                   | 150              | 1.336                    | 0.955                    | 75                 | 100                | 37.38842            |
| 16min             | 25               | 17.90                    | 16.17                    | 320                | 170                | 9.66                |
|                   | 50               | 15.590                   | 14.14                    | 260                | 200                | 12.44528            |
|                   | 100              | 13.940                   | 12.19                    | 190                | 200                | 11.47770            |
|                   | 150              | 11.830                   | 10.12                    | 145                | 110                | 13.7527             |
| 24min             | 25               | 27.22                    | 15.20                    | 140                | 80                 | 43.7                |
|                   | 50               | 16.680                   | 12.88                    | 140                | 90                 | 19.3                |
|                   | 100              | 10.500                   | 9.23                     | 160                | 120                | 12.09524            |
|                   | 150              | 5.950                    | 4.77                     | 150                | 140                | 14.66905            |
| 30min             | 25               | 36.780                   | 35.09                    | 220                | 200                | 4.64                |
|                   | 50               | 23.360                   | 21.97                    | 160                | 180                | 5.80                |
|                   | 100              | 18.580                   | 15.85                    | 140                | 150                | 9.80058             |
|                   | 150              | 9.520                    | 6.63                     | 150                | 140                | 9.82250             |

1. Resistance –time characteristic of sensor without gas.

The resistance of the PSi layer between the deposited metallic electrodes in the case of absence of CO₂ gas molecule varied according to the etching time, illumination wavelength, and the operating temperature. From the Tables 2 and 3 we can list the following facts:

1-For fixed type of PSi sample, the resistance of the PSi was increases with increasing the etching time. This behavior is due to the quantum confinement effect for the charge carrier in the depletion process. This will lead to decreases the effective charge carriers which contribute to conductance process in PSi layer. The increasing of these bonds and the effects of depletional charge carriers would lead to the increase the charge depleted region (w) according to the passions equation. So the central silicon channel would be dropped to large extent.

2-The resistance of IR illuminated PSi gas sensor samples in general was less than that of violet illuminated samples due to the fact that the density of the dangling bonds Si-H, and Si-O-Si.
Resistance –time characteristic of sensor with presence of gas.

The resistance of PSi layer in the presence of gas CO$_2$ molecule as a function to the time was varied according to the type of PSi layer. Also the sensitivity, the response time, and recovery time depended on the PSi layer. The following facts can be deduced.

1. The sensitivity of IR illuminated PSi samples was higher than that of the violet illumination PSi gas sensor samples.

2. At fixed etching time the response time PSi gas sensor was slightly varied with increasing the operating temperature from (25-150°C).

3. For fixed etching time the recovery time was often higher than the response time for both PSi substrate, including a fast rate for adsorption than for desorption of CO$_2$ gas from the porous matrix. For the performance of the fabricated porous silicon planer structure, we have realized a sensor which the resistance decreased down to (one or two order) of magnitude in the presence of carbon dioxide. To interpret quantitatively this behaviour, we discussed the performance of the sensor according to the activity of the dangling bonds (Si-H) associated with porous silicon. Based on the D. stievenard and Deresmes model [22]. The conductivity and hence the resistivity was governed by width of the channel resulting from the partial depletion of silicon located between pores. This partial depletion region was resulting from the charges trapped on the surface states associated with the partially oxidation of porous silicon (Si-SiO$_2$) where SiO$_2$ was the native silicon oxide. In order to explain the electrical behaviour of the sensor, we proposed the following schematic representation (4.28). Due to the partially oxidation of PSi which occurred spontaneously during aging process, there was a thin layer of SiO$_2$ and associated interface states having density ($\delta$) cm$^{-2}$, there was a depleted region in the silicon material over the region(w). So the effective silicon channel has a width ($d-2w$) in which the carriers can move when the applied voltage was applied on the planer junction[23].

\[ w = \delta / N_D \]  

(10)

Where $N_D$ is the doping level in the silicon. So the conductivity of the sensor was govern by ($\delta$). The effect of the gas was to passivate the active dangling bonds through screening mechanism, so that ($w$) decreases and the width of the channels increases. In our samples, $d$ is the order (0.7µm). The density of the dangling bonds was about $10^{12}-10^{13}$ cm$^2$. As the initial doping of Si was in the order of ($4.1*10^{14}$ cm$^{-3}$), there were enough DB to passivate the free carriers. We found that ($w$) was in the order of ($0.02*10^{-14}$nm) so the central channel can be easily pinched.

5. Conclusions

PSi based gas sensor substrate were fabricated by photo–electrochemical etching process the sensitivity will modify according to the porous silicon morphology. Higher sensitivity was obtained. The maximum porosity with lower porous layer thickness was obtained with violet illuminated PSi sample rather than the IR illuminated PSi sample. The IR illuminated PSi layer has surface morphology of pore- like structure at etching time ranging from(5-20min), while violet illuminated PSi layer has surface morphology of cross- like structure with different sizes. The gas sensor performance was chanced according to the gas sensor configurations and characteristics of the porous layer. The porous silicon gas sensitivity was increase with increase the pore size within the porous layer. Efficient porous silicon gas sensor can be fabricated in sandwich configuration mode from a thin porous layer rather than thick porous layer.
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