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Study of the Influence of Incorporation of Gold Nanoparticles on the Modified Porous Silicon Sensor for Petroleum Gas Detection

Abstract- In this work, the influence of alloying the porous surface with uniform distributed gold nanoparticles on the characteristic porous silicon gas sensors for petroleum gas detection has been fabricated and studied extensively. Well-controlled gold nanoparticles were prepared by employing the simple dipping process of the macro porous silicon surface in diluted concentrations of HAuCl_4 salt aqueous solution. The sensing properties of the prepared porous silicon-based sensors, sensitivity response and recovery times at room temperature operating in CO gas were studied. The sensitivity of alloyed porous silicon increased from 38% to about 82% incorporation of gold nanoparticles. The lowest gas pressure detection process of CO molecules was improved from 1 mbar to 0.5 mbar. The surface alloying with rounded gold nanoparticles improved the integrated specific surface area of the alloyed porous silicon/gold nanoparticles structure, so efficient gas developed with the low-cost process.

Keywords: gold nanoparticles, SEM, porous silicon, gas detection

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1. Introduction

Porous silicon is a promising material for a wide variety of applications ranging from gas sensing to chemical detection. The physical properties of the porous sample have been observed to change in the presence of inorganic gas like CO. The detected conductivity of porous silicon (Psi) undergoes changes as gaseous molecules are absorbed on its surface [1].

Among a large group of organic gasses during the production of petroleum, the carbon monoxide has a significant health impact on humans. Traditional methods of CO detection usually rely on the change in the refractive index of porous silicon surface as the CO gas molecule fills up the pores [2-4]. The drawback of this method is related to its inability to distinguish the very low concentration of gasses; this is because their refractive index would change depending on how many of the pores were filled up [5].

The carbon monoxide (CO) is normally classified as inert gas inters of an acid-base reaction. The output signal from the untreated porous silicon sensor is a weak signal. The surface treatment of porous silicon with TiO_2 and SnO_2 will improve the output signal from the sensor and hence enhancing the sensing capabilities. Surface modification of PSi by incorporating gold nanoparticles has been found to be a potential

method to enhance the sensing capabilities for low concentration CO molecule. In this paper, a study on the fabrication of AuNPs/Psi hybrid structural of CO gas sensing was carried out to improve the detection capacities for very low concentration CO molecule [5,6].

2. Fabrication and Experimental

As-formed porous silicon substrates gas sensor was made-up by means of the n-type silicon substrate of (100) orientation, and resistivity of about (100 Ω . cm). The silicon substrates were cut into dimensions at (2 \times 2 cm) and etched through a laser-assisted etching process.

The silicon substrates have been washed using high purity 99. 9% ethanol. The silicon substrate acts as the anode, while the cathode was a ring of Platinum (Pt) and immersed in 15% hydrofluoric acid (HF) concentration. The Continuous Wave laser diode of the wavelength of (400nm), the intensity (50mW/cm²) with an etching time of about 30 min were used as presented in Figure 1 [7].

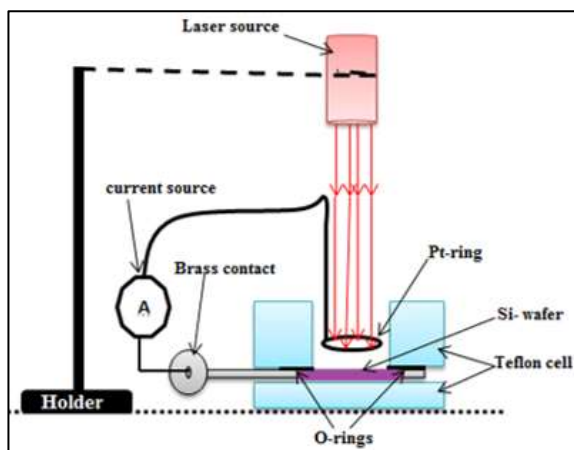
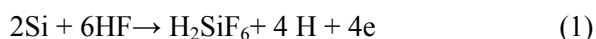


Figure 1: experimental setup laser- assisted etching process [7]

After the preparation of porous silicon substrates, the gold nanoparticle (AuNPs) was deposited on a porous layer by an ion reduction process by dipping the interface into aqueous solutions of HAuCl_4/HF acid, with (0.5mM/3.5M) at room temperature. The ion reduction process of AuNPs by the dangling bonds of the porous layer given by the equation [7]:



The sensor was fabricated by deposition of Aluminum film thickness of about 30 nm onto the golden porous silicon surface and the bottom layer of porous silicon substrate was coated with thick Aluminum layer as an electrode to synthesise a sandwich structure of (ALthin/AuNPs/ nPSi/n-Si/AL electrode) as presented in figure (2). The current - voltage characteristic was carried out in the dark condition of DC power supply and electrometer device (Keithly 610C) [8].

After the fabrication of the sensor, it was tested with gas pressure (1 m bar to 0.5 m bar) of CO gas. The measurement was carried out at room temperatures. Figure (3) shows the gas-sensing setup of porous silicon sensor performance. The current – voltage characteristics were done in a small closed dark chamber with inlet and outlet to gas detection.

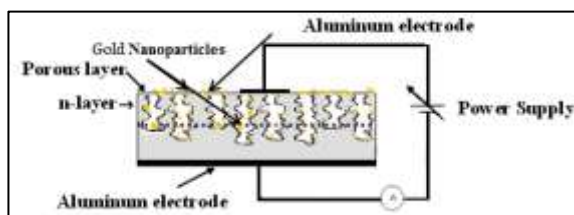


Figure 2: cross-section of (ALthin/ AuNPs/ nPSi/n-Si/AL electrode) structure gas sensor with electrical contact [8]

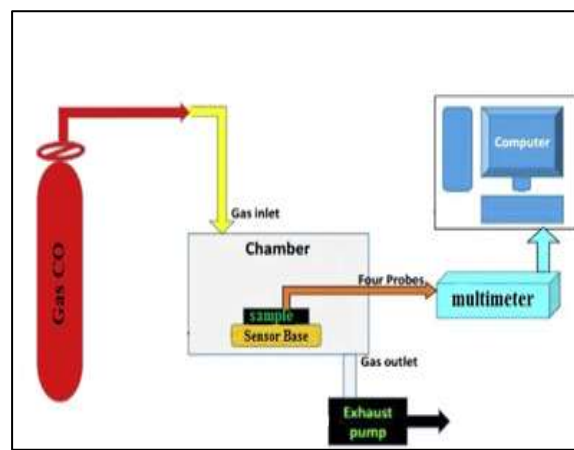


Figure 3: represents schematically of the sensing measurement

3. Results and Discussion

Porosity as formed reflects one of the key factors that describe the surface morphology. The porosity of porous silicon substrate samples measured through gravimetric method [8] was about (81%).

Figure 4 illustrates the surface morphology of as-formed macroporous silicon surface substrates like (pore size and pore shape) while allowing porous silicon surface with gold nanoparticles are investigated by analysis of high-resolution scanning electron microscopy images and the statically particles diameter distributions were presented in Figure 5a, b. This analysis based on the SEM images of porous silicon substrates showed that the surface of the porous layer looks like pore-like structure consisting of two types of pores shape rectangular and gambling forms with randomly distributed over the surface, the diameter of the pores is ranging from (4.5 μm) to (8.3 μm) The major value of the pore sizes may possibly attribute to accumulative of e-h pairs inside the porous layer, which improve the silicon dissolution process between the nearest-neighbor pores [9].

The Gaussian distribution of the laser beam power density leads to make the silicon etching rates have different values and therefore causing in a porous layer with different pore size. The SEM images of gold nanoparticles showed that its shape was mostly rounded gold nanoparticles with different sizes ranging from 25nm to 135nm and peak of particle diameter distributions is about 120nm as shown in Figure (5b).

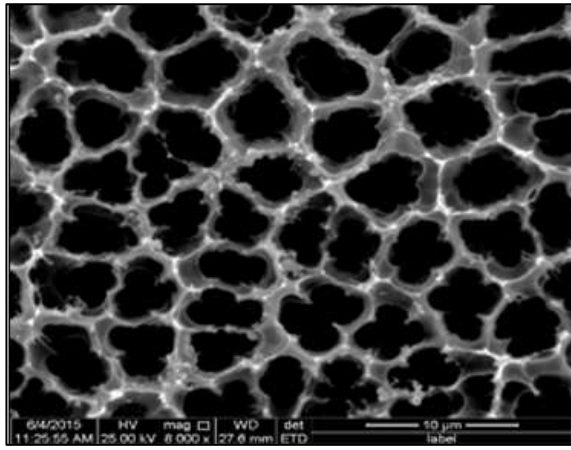


Figure 4: shows the SEM images of as-formed porous silicon substrates

Figure 6 illustrates the XRD analysis of alloying porous silicon surface with gold nanoparticles. From this figure its clear to us that the porous silicon still crystalline nature in the plane (100) with a specific diffraction angle of about (32.4°). The deposited AuNPs on the porous layer shows specific Bragg's reflections at diffraction peaks at an angle of (38°) and (44.4°) for the planes (111) and (200) respectively, these peaks are the finger of print of FCC crystal lattice of pure Gold. The sensing mechanism of alloyed porous silicon within a structure of AL thin/ AuNPs/ nPSi/n-Si/AL electrode structure gas sensor and as-formed porous silicon substrates without of incorporation of gold nanoparticles are based on the response of the current –voltage Characteristics.

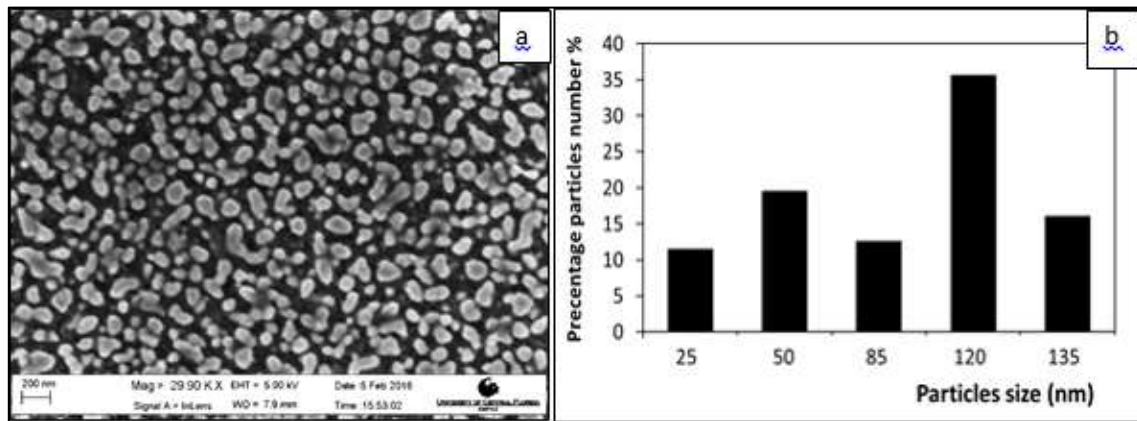


Figure 5 Presents a) SEM images AuNPs, b) The statically particles diameter distributions

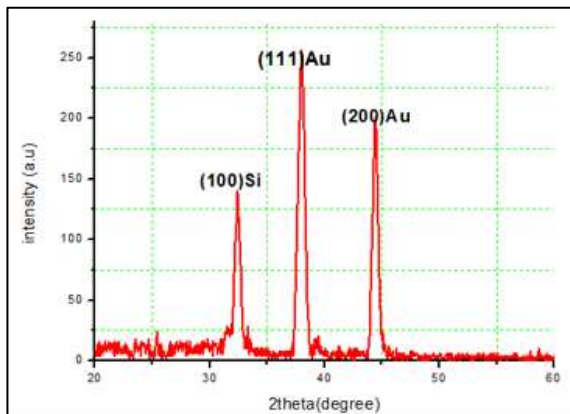


Figure 6: presents XRD pattern of alloying porous silicon surface with gold nanoparticles

Figures 7 and 8 display the current –voltage Characteristics of the fabricated gas sensors at room temperature and all measurements were taken in the dark with applied voltage ranging from 0 to 5v. In AL thin/ AuNPs/ nPSi/n-Si/AL electrode) prepared device, the forward current –voltage behavior Figure 8 follows as Schottky [10], while for as-formed porous silicon substrates without of incorporation of gold

nanoparticles as shown in Figure (7) the characteristics exhibit a linear relationship depended on the properties of the porous layer and the total current of the device is controlled by carrier transport in the high resistivity. The growing of the current in the attendance of CO gas due to adsorbate interaction with porous silicon dangling bond, is mainly related to boost the conductance variations due to the trapping or release the carriers [11]. Additionally, the surface alloying with rounded gold nanoparticles improved the integrated specific surface area of the alloyed porous silicon/gold nanoparticles structure and hence increase the gas adsorption rate [12]. The response of the current of the sensor (S) is calculated by the following relation (3) in terms of current instead of the resistance due to the fact that the device is operated in sandwich form rather than the planar form:

$$S = \left| \frac{I_{\text{gas}} - I_{\text{air}}}{I_{\text{air}}} \right| \quad (3)$$

Where I_{gas} and I_{air} characterize the current in the attendance and absent of CO gas respectively [11]. The sensitivity of alloyed porous silicon increased from 38% to about 82% incorporation of gold nanoparticles.

Figures 9 display the successive current responses with time when CO gas at a pressure of 0.5 and 1 m bar. For sensors, AL thin/ AuNPs/ nPSi/n-Si/AL electrode) structure gas sensor and as-formed porous silicon substrates without of incorporation of gold nanoparticles, both adsorption and desorption times were set 3 min. Fresh air was flown in the cavity. The response time is Well-known, as the time required the sensor to reach 90% of maximum current from early value while the recovery time is well defined as the time taken from maximum current to reach 10 % of its maximum current value [12]. From the figure, both in response and recovery times were less for AL thin/ AuNPs/ nPSi/n-Si/AL electrode sensor compared with as-formed porous silicon substrates sensor.

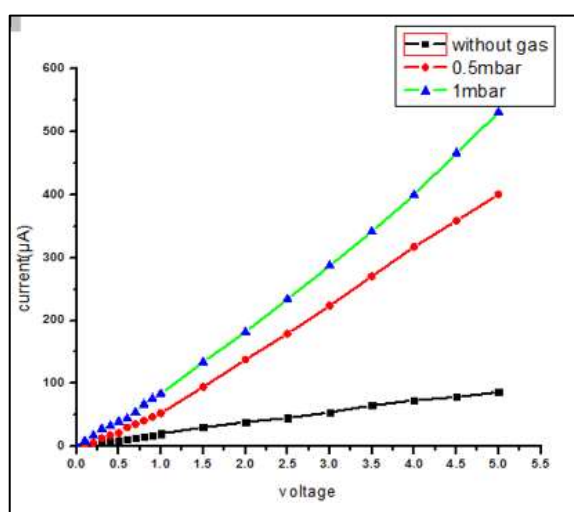


Figure 7: illustrated the current –voltage characteristics of as-formed porous silicon gas sensor without of incorporation of gold nanoparticles under CO gas at a pressure of 0.5 and 1 m bar

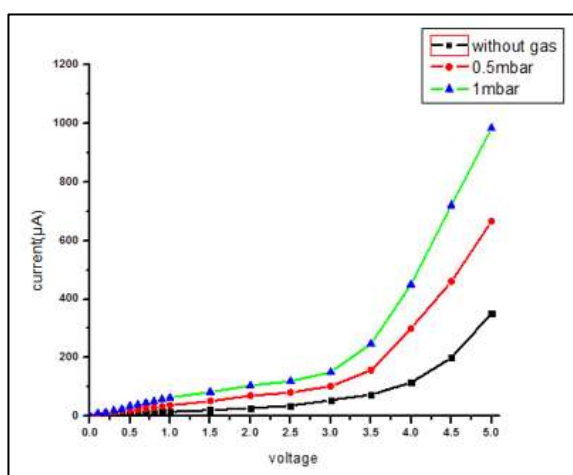


Figure 8: illustrated the current –voltage characteristics of AL thin/ AuNPs/ nPSi/n-Si/AL electrode) structure gas sensor under CO gas at a pressure of 0.5 and 1 m bar

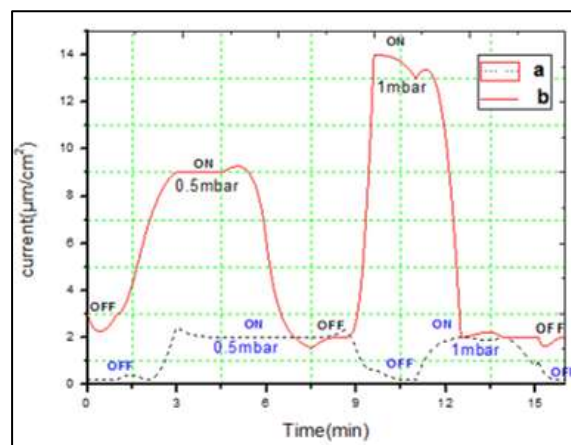


Figure 9: illustrated the current –voltage characteristics of AL thin/ AuNPs/ nPSi/n-Si/AL electrode) structure gas sensor under CO gas at a pressure of 0.5 and 1 m bar

3. Conclusions

In this work, a well-controlled gold nanoparticle was used to fabricate an efficient alloyed porous silicon gas sensor for Co molecules. The alloying process of macroporous morphology was carried out by a simple dipping process of macro porous in diluted concentrations of HAuCl_4 salt aqueous solution. It was shown that the sensor response depends strongly on the deposited gold nanoparticle. The AL thin/ AuNPs/ nPSi/n-Si/AL electrode sensor shows a high sensitivity for detection the low concentrations of CO gas (1 mbar to 0.5 mbar) of about 82% compared with 38% for as-formed porous silicon gas sensor. The surface alloying of porous silicon with rounded gold nanoparticles demonstrates an encouraging process in the field of gas detection.

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