Chapter

A Novel Sensing Method for VOCs Using Nanoparticle-Coated Nanoporous Silicon

Selvakumar Varadarajan Subramani, Suganthi Selvakumar and Sujatha Lakshminarayanan

Abstract

Structural aspects, such as grain size, pore size, and crack-free film morphology, of porous silicon (PS), etc., play a vital role in the sensing of volatile organic compounds (VOCs). This chapter discusses a novel method for sensing of VOCs using porous silicon coated with a layer of ZnO (PS-ZnO). It was noted that the sensing ability of the PS sensor has increased due to the transconductance mechanism, as a result of the coating of ZnO over PS. Initially, porous silicon is formed by electrochemical wet etching of silicon and by electrophoretic deposition (EPD), ZnO is coated over porous silicon. An increase in the selectivity is due to the increase in surface-to-volume ratio and uniformity in the pore structures. The thickness of ZnO layer can be tuned up to 25 nm by applying a DC voltage between the copper electrode and the conductive silicon substrate immersed in a suspension of ZnO quantum dots. The influence of quantum dot concentration on the final layer thickness was studied by X-ray diffraction (XRD). The change in resistance for ethanol was found to be 12.8–16 MΩ and 8–16 MΩ for methanol.

Keywords: porous silicon, VOC sensing, metal oxide coating, electrochemical wet etching

1. Introduction

Porous silicon (PS) is a vital medium, which can be fabricated easily by electrochemical etching of silicon in HF acid solution [1]. The surface area of PS can be up to million times than that of a planar silicon surface. The melting point of silicon is lowered due to this high surface area [2]. Due to its characteristics such as high surface area and high chemical activity, it is popularly used as sensors to detect gases like NO_2, NH_3, H_2S, SO_2, ethanol, and acetone [1–3]. Compared to other semiconductor-based gas sensors (SnO_2, CuO, Cr_2O_3, and V_2O_5), PS-based gas sensors operate at comparatively lower temperatures, even at room temperature (RT) [4]. Furthermore, PS manufactured by the semiconducting material is compatible with silicon IC technology that provides the possibility to integrate the PS-based sensing element into any device [4–6]. This makes PS a promising gas-sensing material. However, the poor sensitivity and low thermal stability limit the industrial applications of PS [7].

Zinc oxide (ZnO) as an instantaneous band gap semiconductor (E_g = 3.37 eV) is used in development of gas sensors, optoelectronic devices, photovoltaic devices, and piezoelectrics [5–8]. Recent observations by Rai et al. have shown that the sensing properties of sensors depend on the morphology and surface-to-volume ratio of the sensing materials [9]. It is believed that ZnO nanostructures have high sensitivity due to their high surface-to-volume ratio and high electron mobility [5–9]. They are already being used for sensing gases such as NO_2, H_2, CO, and ethanol [5–12]. ZnO can be prepared in RT through electrophoretic deposition (EPD) of a colloidal suspension of quantum debris. EPD has been widely used to deposit particles within the micron size [13, 14]. Moreover, compared with the other processing methods, EPD is able to produce uniform deposits with high microstructural homogeneity. This helps us to control the deposit thickness and in depositing coatings on a broad range of patterns [15–17]. However, the high operating temperature and high power consumption of ZnO-based gas sensors limit its application.

The presence of a certain gas can be detected by the change in resistance produced in the sensor due to the adsorption of the analyte molecules by the PS film [18, 19]. In this chapter, we have discussed the fabrication procedure and the sensing mechanism of VOCs by PS-based gas sensor coated with ZnO (PS-ZnO) nanoparticles. The sensitivity, selectivity, and repeatability of the PS-ZnO sensor are also discussed. The primary grail of this research is to bring up a competitive impedance metric analysis of a two-point metal contact on PS-ZnO-based VOC sensor.

2. Experimental setup

2.1 Fabrication of PS-ZnO-based VOC sensor

Figure 1 shows the cross-sectional view of PS-ZnO-based VOC sensor. Since the ethanol sensing mechanism involves the formation of two layers (ZnO and PS), the following steps are followed in the manufacturing process:

1. Surface planning or silicon wafer (10 ohm-cm) cleaning

2. Electrochemical wet etching of silicon

3. Formation of permeable silicon (couple of hundred nanometer)

4. Deposition of ZnO by electrophoretic deposition

5. Making Al contact terminals utilizing screen printing system

6. Constructing the test chamber for location of ethanol, alcohol, and methanol vapor utilizing potential analyzer

The first step in the manufacturing process involves the preparation or cleaning of the silicon wafer. It is done to expel the organic and inorganic impurities that may be present on the substrate. The standard procedure followed is the RCA clean method. It is a procedure that must be performed before electrochemical wet etching.

Initially in the RCA cleaning process, organic cleaning is used to remove the natural contaminants present in thesilicon. This process is called organic clean method. The chemicals used in the organic clean process are added in the ratio of 1:1:5 corresponding to $NH_4OH/H_2O_2/H_2O$. After the initial step, ionic impurities

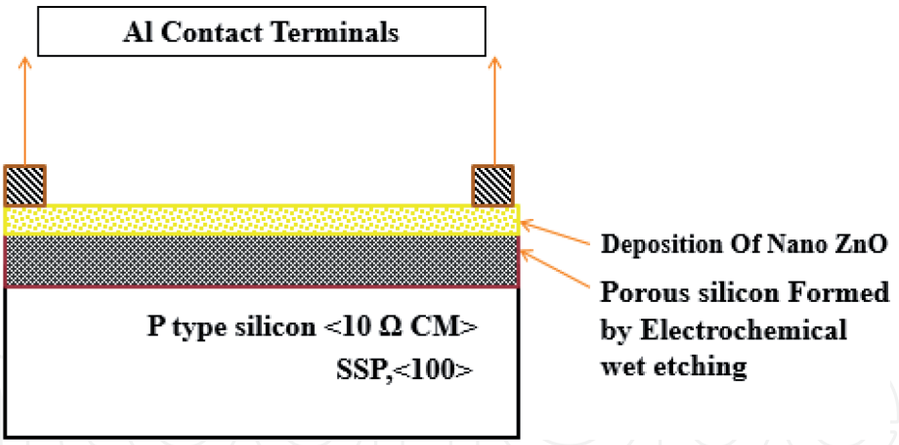


Figure 1.
Cross-sectional view of PS-ZnO-based sensor.

(ionic pollutants) are removed by a process called ionic clean method. Here the cleaning solution is in the ratio 1:1:6 corresponding to $HCl/H_2O_2/H_2O$. Once the ionic impurities are removed, the wafer is washed with deionized (DI) water, and it is later dried with the help of N_2 gas. Now the wafer is submersed in a 1:50 arrangement of HF + H_2O at 75°C usually for 10 minutes, which helps to eliminate the thin oxide layer and some of the ionic contaminants. Finally, the wafer is again flushed in a solution of deionized water and dried again by nitrogen gas.

2.2 Formation of porous silicon (PS)

The second step is the manufacturing process in the formation of the porous silicon. The initial material is a solitary crystalline silicon of p-type substrate with 1–10 ohms-cm resistivity, <100> orientation, and 525 μm thickness and is polished on one side. Initially the surface cleaning process has been done as mentioned in the previous step in the manufacturing stream. After which, the wafers have been cut into rectangular bits of 2 × 2 cm to give a uniform current distribution over the surface of the substrate. A layer of aluminum is then deposited on the bottom the silicon specimen by means of thermal evaporation.

The experimental setup for the preparation of the porous silicon can be seen in **Figure 2**. Initially, the silicon sample has been put at the base of a round and hollow Teflon cell and is properly adjusted by a tempered steel plate which acts as a support material. The cell has two electrodes as shown. The silicon wafer is considered or used as an anode, and a platinum rod placed in a HF safe material is utilized as a cathode. In our trials, the Pt mesh which acts as the cathode was taken and set vertically opposite to the anode at the highest point of the cell. The space of the cell between the two electrodes is filled with the HF-based electrolyte. The electric flow is provided by the presence of a DC steady flow source which is used to connect the two electrodes. When there is a current flowing through the circuit, the cathode excites electrolytic solution which leads to the etching of numerous small pores on the surface of the anode (Si), thus leading to the formation of porous silicon.

The porosity of PS is proportional to the current density between the electrodes and the time of the process. To attain 65% porosity, it took up to 6 minutes at a current density of 5 mA/cm^2. To attain a porosity of 75%, in our case, it took 10 minutes at a current density of 15 mA/cm^2. After the successful formation of the porous silicon, the sample specimen was tested for photoluminescence by several experiments with ethanol and isopropyl alcohol.

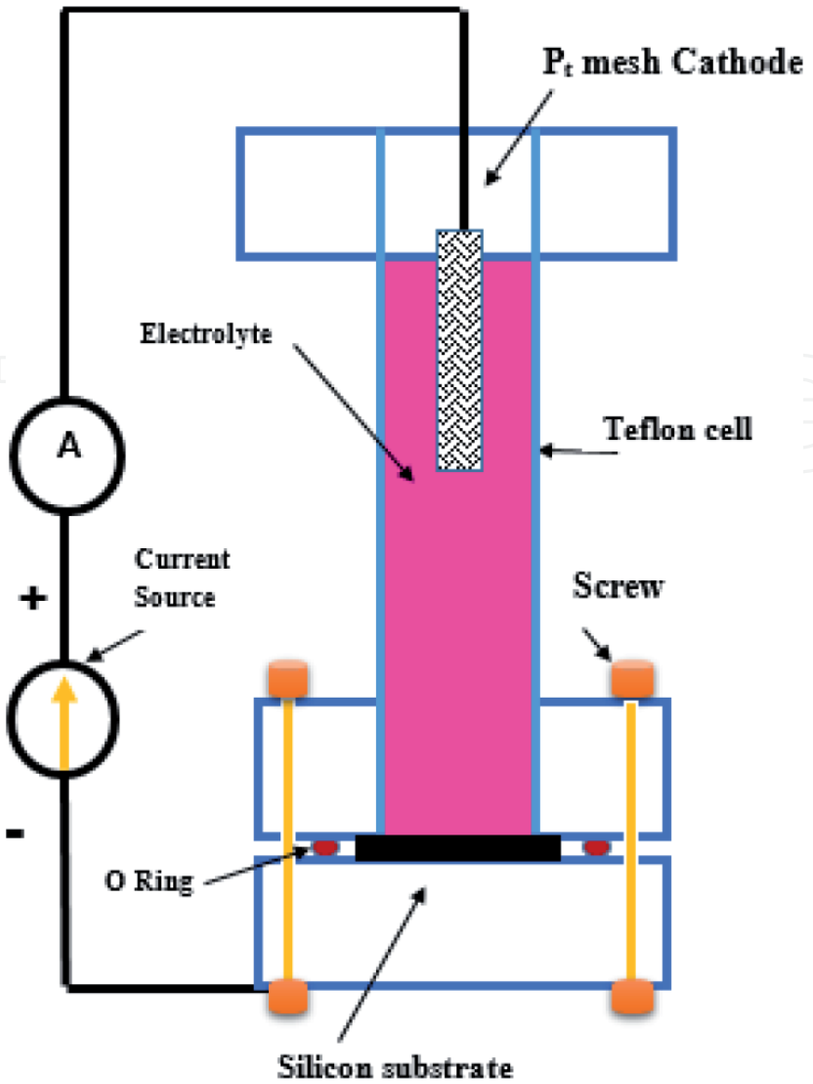


Figure 2.
Electrochemical wet etching of silicon.

From our observations described in the **Table 1**, we concluded that the photoluminescence property could be checked by the UV detection method. The UV photo illumination of porous silicon demonstrates that the reflected UV photography is excited by UV-transmitting LEDs or devices (radiation sources) or by solid daylight. A UV-transmitting channel is placed on the focal point, which enables bright light to pass and collects all visible and infrared light.

2.3 Selection of sensing materials

For optimal sensing performance, the sensing material to be selected should be carefully considered. The material selection is based on the operating temperature, range of detection, response time, sensing form, sensing parameters, and processing compatibility of the target VOC. Three materials—SnO_2, TiO_2, and ZnO—satisfy all the above parameters for the detection of VOC. However, among these three, ZnO operates at room temperature, which means that there is no need for a heating element. It also has a faster response time of less than a second and is silicon processing compatible. On the other hand, TiO_2 has a slow response time of about 3 minutes and operates only at 200–400°C. In addition, SnO_2 has a narrow range of detection and slower response time. The selectivity of SnO_2 is also less. Due to these reasons, we select ZnO as the sensing material.

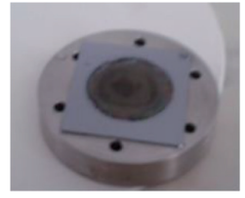
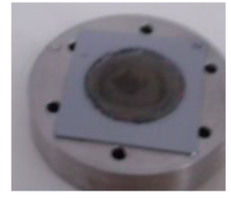
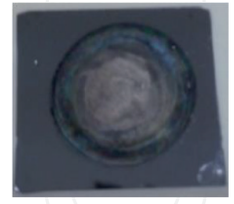
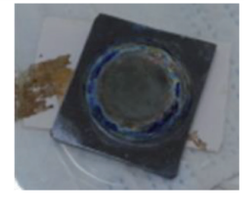
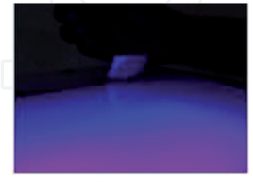
S. No	Name	HF/ethanol	HF/IP	HF/IP	HF/IP
1.	P-type silicon	1	1	1	1
2.	Area	2.009 cm^2	2.009 cm^2	2.009 cm^2	2.009 cm^2
3.	Current density	5 mA/cm^2	5 mA/cm^2	7.5 mA/cm^2	10 mA/cm^2
4.	Current across anode and cathode	8 mA	10 mA	15 mA	20 mA
5.	Electrolyte	(3:7 (10 ml)	1:2 (10 ml)	1:2 (10 ml)	1:1(10 ml)
6.	Pt mesh cathode	1	1	1	1
7.	O ring	1	1	1	1
8	After experiment				
9	Photo luminance property checked by UV detection	No photo luminance	No photo luminance		

Table 1.
Different experimental results with photoluminescence.

2.4 Electrophoretic deposition of ZnO on PS

After the successful manufacturing of the porous silicon specimen, a thin layer of ZnO had to be deposited on the surface of the substrate by means of electrophoretic deposition (EPD). The mechanism of the EPD process is illustrated in **Figure 3**. A glass vessel was used for this experiment. The PS material to be coated was taken as the anode, and we utilized an aluminum rod as a cathode. The two electrodes were submerged in a solution of isopropanol which had numerous ZnO molecules suspended at the bottom of it. The apparatus had been equipped with a magnetic stirrer placed below the glass vessel which was used to stir the solution at high speeds. A DC voltage had been applied between the two electrodes which caused an electrochemical reaction between the two submerged electrodes. Initially, the suspended particles in the isopropanol were released due to the magnetic stirring process. Once the ZnO molecules start floating in the solution, the voltage caused the aluminum anode to repel the colloidal ZnO molecules, and the PS attracted them, causing a migration of particles from the positive to the negative anode, thus creating a thin layer of ZnO coating on it. After deposition, the samples were rinsed with deionized water and were air-dried with N_2 gas.

2.5 Experimental setup for VOC detection

The device was successfully fabricated and was tested for VOC detection. **Figure 4** shows the experimental setup of VOC detection by using PS-ZnO. The testing phase was conducted in an enclosed testing chamber. The specimen to be examined (PS-ZnO) was placed inside, and the chamber was tightly sealed. The chamber had been equipped with an electronic temperature controller attached to it, which regulates the temperature inside the chamber with the help of a heater coil wound around the chamber. The temperature of the coil was measured as well by means of an external thermometer to compare the actual temperature with the regulatory temperature.

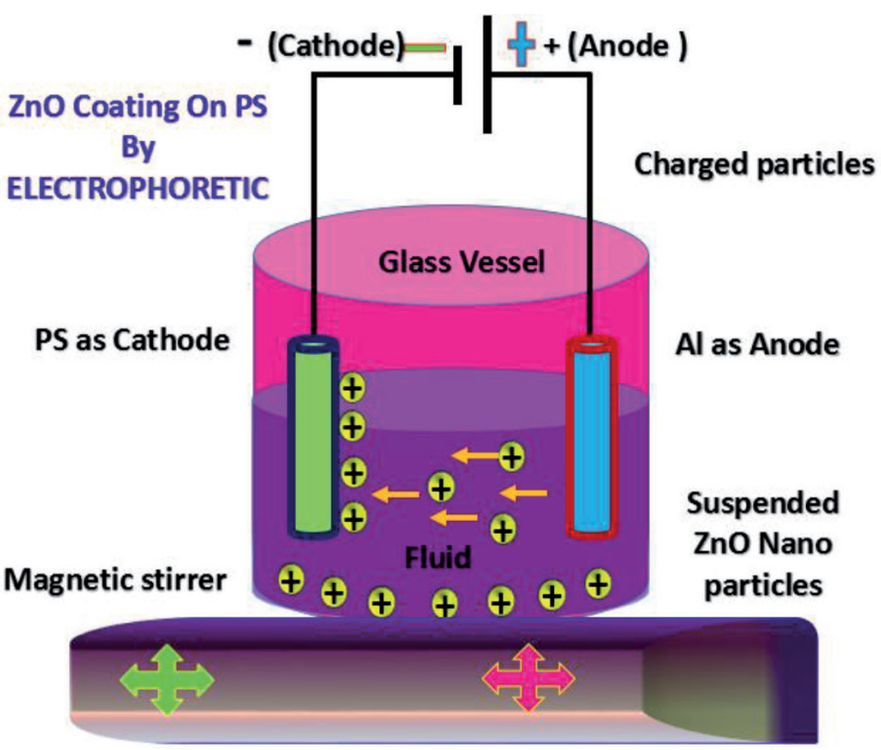


Figure 3.
Illustration of the cathodic electrophoretic deposition process.

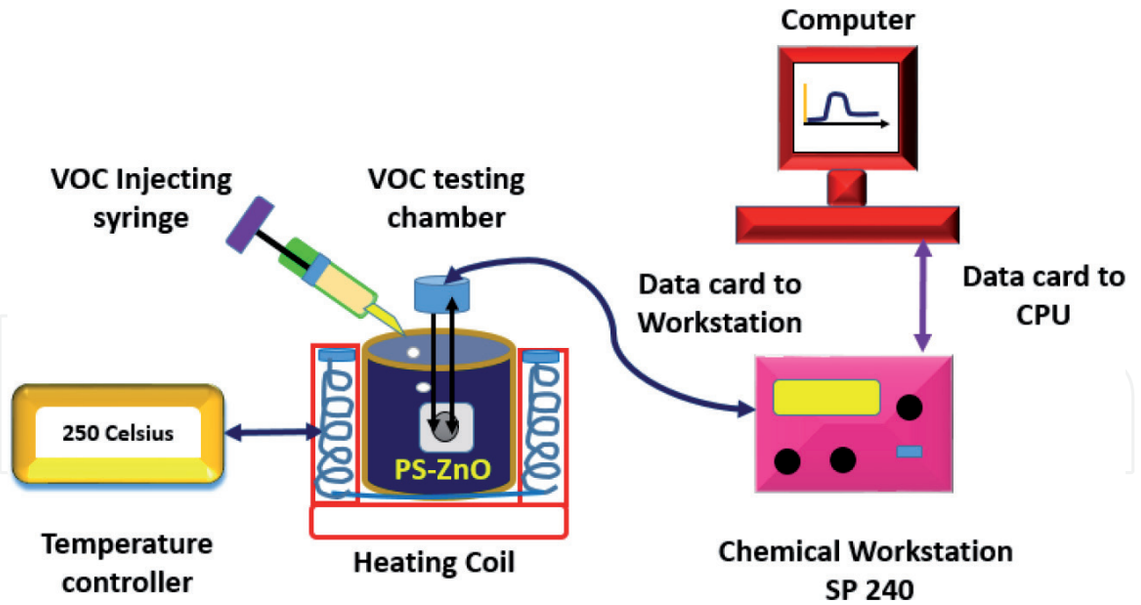


Figure 4.
VOC recording system through chemical workstation.

For our study we had set the regulated temperature in the chamber to 250°C. A data cord was then connected from the testing chamber to a chemical workstation (SP 240). The chemical workstation was then further connected to a CPU to observe readings. The VOC compound to be tested was taken in a syringe and was slowly injected into the gas testing chamber. The injection of the compound was done in a gradual manner, and the corresponding data (impedance characteristics) on the display were observed and noted.

3. Results and discussion

The pictures below in **Figure 5(a)** and **(b)** show the structure of porous silicon before and after the electrophoretic deposition of ZnO on its surface, respectively. The images were used to illustrate the basic topological differences in appearance and structure of the PS substrate between the two stages. The microscopic images of micro PS samples shown in **Figure 6** were used to study the morphology of the substrate after the addition of the ZnO layer. The bright-field microscopic images clearly show

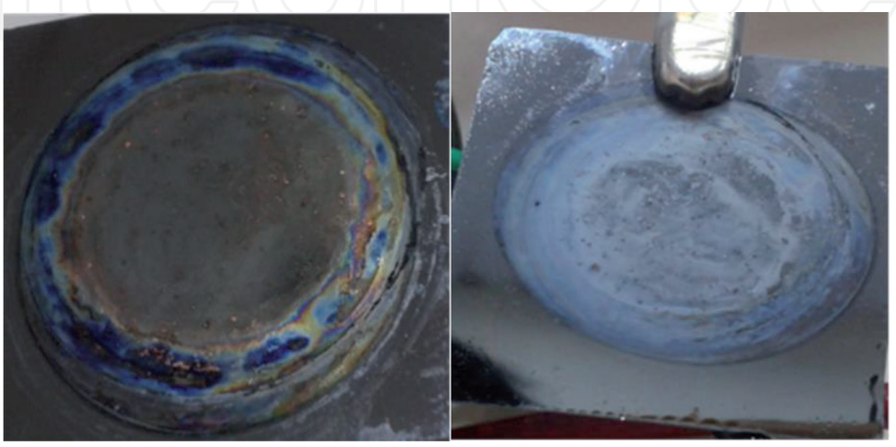


Figure 5.
(a) PS before ZnO deposition by EPD; (b) PS after deposition of ZnO by EPD.

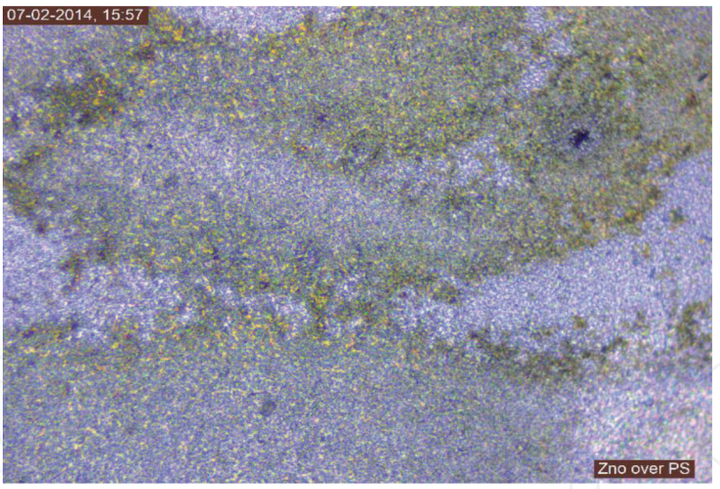


Figure 6.
Microscopic image of PS with ZnO.

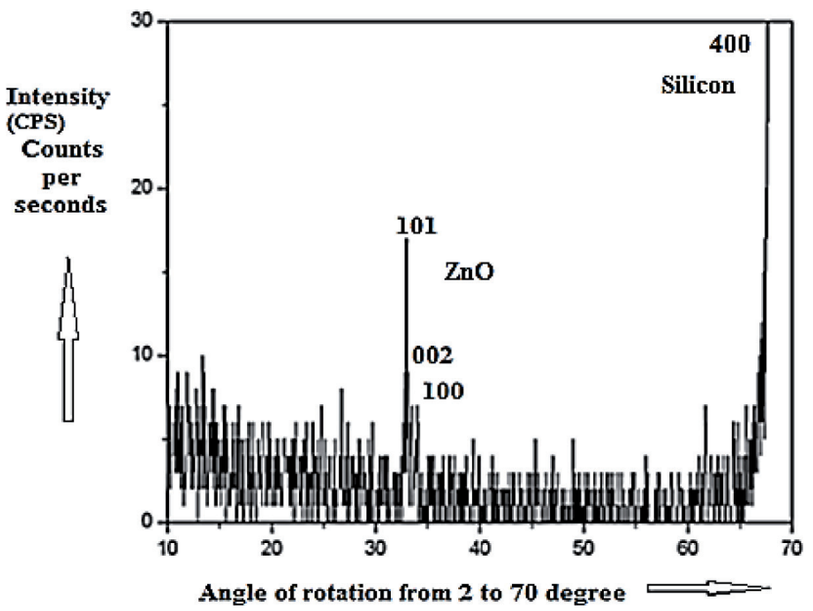


Figure 7.
XRD conformation of ZnO and silicon.

the structural changes in the obtained porous silicon after the coating of ZnO by EPD process. It is observed that the pore sizes are in the order of nanometers. In addition, the pores in micro PS are random in nature with uniform deposition of ZnO.

The coating characterization of the device was tested using spectrum diffraction analysis of both the materials. **Figure 7** shows the conformed X-ray diffraction (XRD) spectrogram of ZnO nanoparticles that are coated on the surface of the PS substrate. Crystalline form of ZnO and PS was taken for the spectrum analysis, and the intensity characteristics were studied by varying the angle of rotation between 2 and 70°. Distinctive intensity peaks of ZnO and the porous silicon material were observed at 32°90′ and 69°8′, respectively. We also observed that the intensity in counts per second (CPS) was much higher for the porous silicon (400) compared to the deposited layer of the ZnO (101).

After studying the coating characterization of ZnO, the sensitivity and the responsivity of the sensor were studied. An impedance study was done with the ZnO-coated PS sensor for certain VOCs, namely, ethanol, isopropanol, and methanol. We also observed the rate-limiting processes that occur at particular frequencies during operation of the device in the impedance spectra.

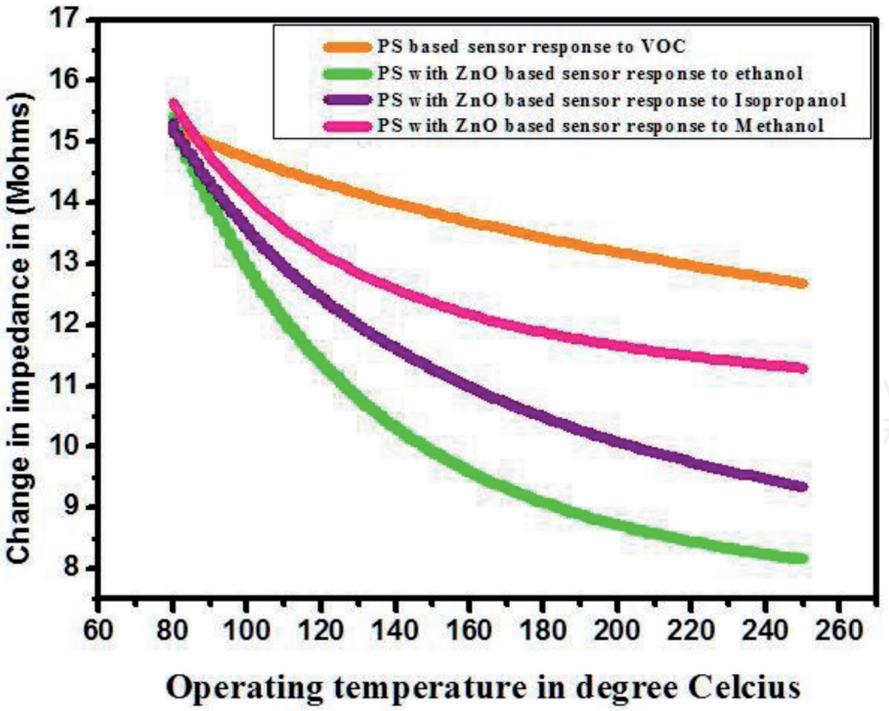


Figure 8.
Sensor response for ethanol, isopropanol, and methanol.

Figure 8 shows a typical Nyquist plot of data recorded from a PS-based sensor with an Al working electrode at room temperature. The plot also shows the results of two measurements made (resistance and temperature) when the sensor was exposed to three different VOCs: (1) ethanol, (2) methanol, and (3) isopropanol. **Figure 8** shows the measure of the change in resistance of the sensor at different temperatures ranging from 70–250°C. It was observed that the change in resistance varied from 8 to 15.8 MΩ for methanol and from 12 to 15.6 MΩ for isopropanol.

The measured change in resistance for ethanol was observed as well which varied from 12 to 15.8 MΩ at the same temperature gradient. We observed that the greatest percentage of change in the impedance measurement for the given temperature range was the highest for methanol. It is also evident that the percentage of change in resistance for the PS-based sensor without the ZnO coating is lower than the device coated with the ZnO film. The result thus proves that the sensing properties of a PS-based device are significantly increased by the addition of ZnO coating.

After observing the impedance characteristics of the device, we tested the responsivity of the sensor for different concentrations of ethanol. **Figure 9** shows the response of the ZnO-based VOC sensor for different concentrations of ethanol at a specific temperature of 250°C. We observed that as the concentration of ethanol kept increasing, the resistance of the device kept decreasing. This gave a linear increase in responsivity from 0 to 255 ppm of ethanol after which the increase in responsivity was relatively less due to saturation of ethanol level. After studying the sensitivity and responsivity of the sensor, the selectivity was studied as well.

Figure 10 summarizes the selectivity of PS toward aliphatic alcohol with respect to various VOCs at a frequency of 100 Hz. We observed that the selectivity of methanol was around 90%, while the same for ethanol and isopropanol compounds was around 50 and 60%, respectively. It shows that the response and recovery of the sensor are about 2 and 27 s, respectively. This indicates the response and recovery performance of the developed sensor toward methanol, ethanol, and isopropanol. The various quick responses and recoveries of methanol, ethanol, and isopropanol

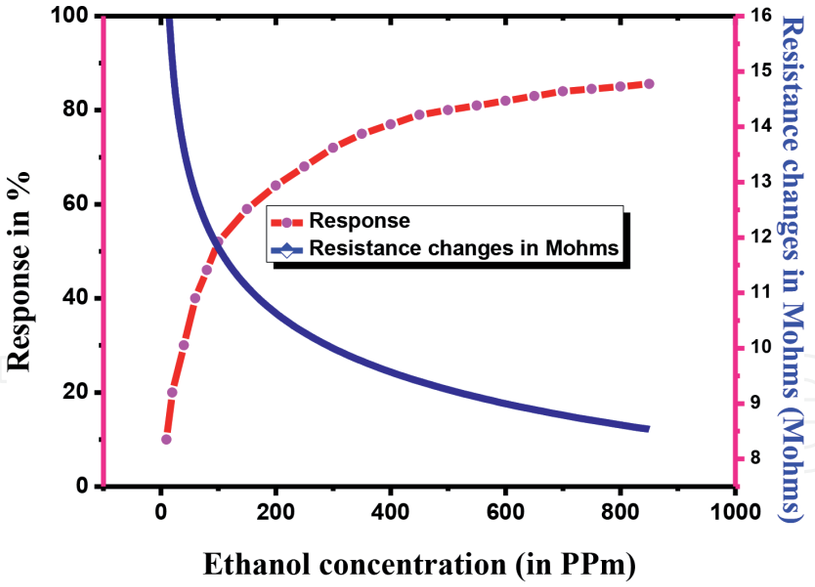


Figure 9.
Response and sensitivity for ethanol concentration.

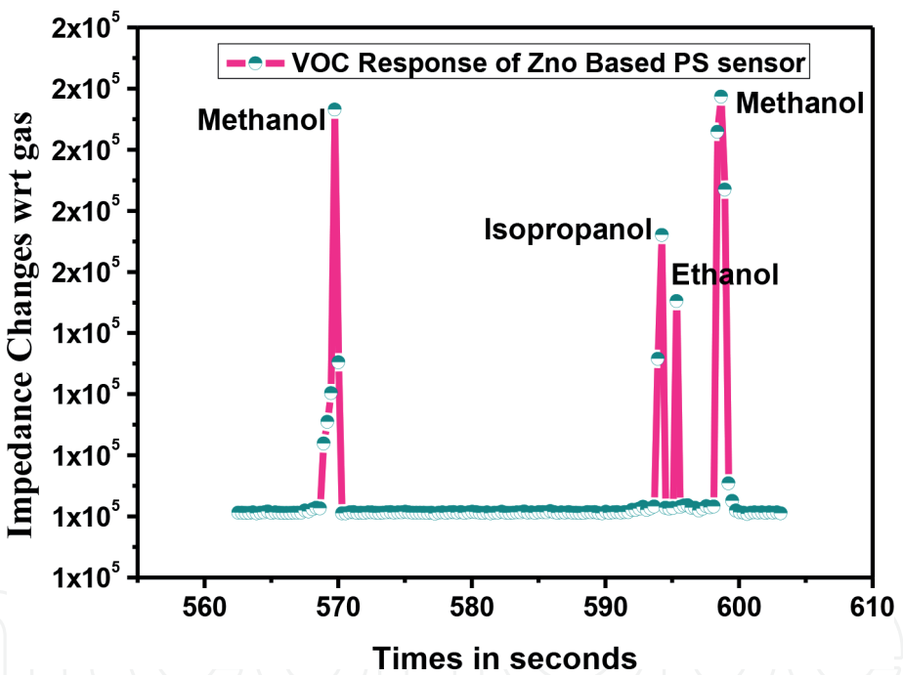


Figure 10.
Sensor repeatability test for different VOC concentrations.

clearly prove selectivity of these VOCs by measuring different impedances. The ZnO-PS-based sensor is very sensitive to methanol when compared to all other VOCs.

From **Figure 11**, it is understood that the selectivity and repeatability are one of the range of acceptable values the sensor will read, relevant to a previous measurement, when measuring a methanol, ethanol, and isopropanol, independent of the actual gas concentration. It clearly shows that the sensing action remains unchanged for repeated measurement.

In the modern world, nanostructured oxide-based VOC sensors are used in applications such as monitoring the environment, chemical process control equipment, and health regulation devices. However, the crux of the operating mechanism is still not completely understood. Therefore, a deeper understanding would be beneficial to

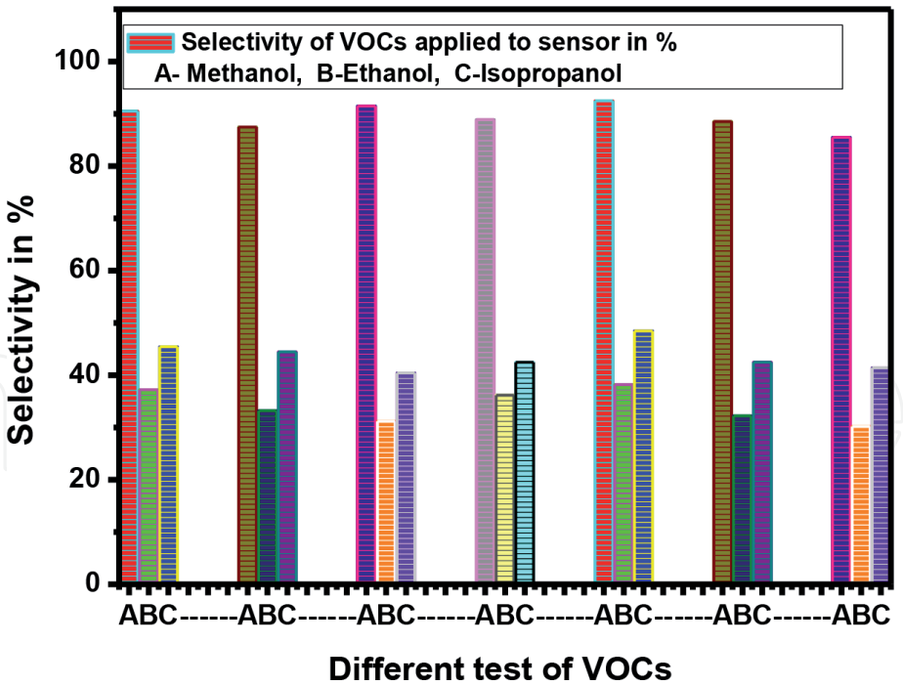


Figure 11.
Sensor selectivity for VOC concentration in repeated test.

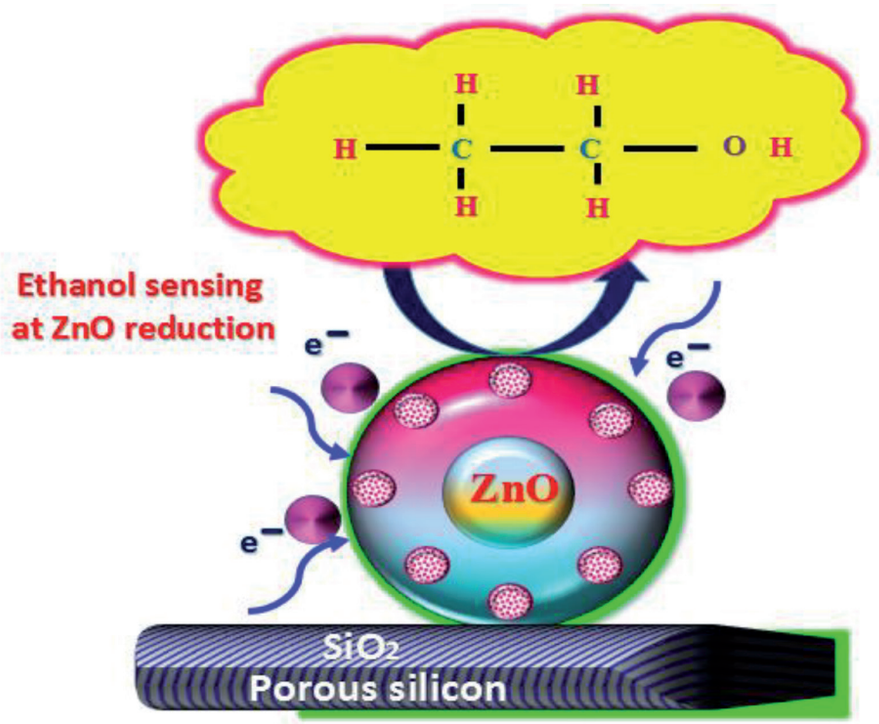


Figure 12.
VOC sensing mechanism of ZnO-based PS sensor.

the development of enhanced sensing elements which can be used for the mentioned applications. In the case of ethanol sensing, our outcomes uncover that the focused adsorption of electrons at the nanostructure surfaces between the porous silicon and the ethanol particles via reduction process (as shown in **Figure 4**) indicates the presence of ethanol at that region. Therefore, the process of ethanol fixating on the ZnO can be identified electronically, helping us discover the sensing element.

Initially, there is an interaction between the ethanol molecules and the chemically absorbed oxygen ions that are present in the sensing element (ZnO). The

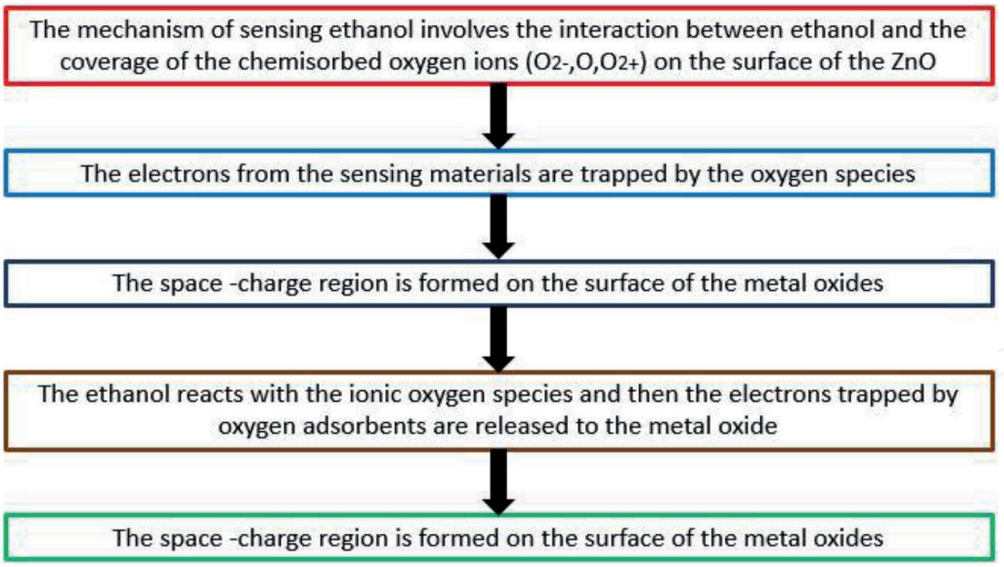


Figure 13.
VOC sensing mechanism of nanoparticle-based PS sensor.

electrons that are present in the sensing material are already trapped by these oxygen compounds or species. Due to this, a surface charge layer is formed on the surface of the metal oxide (ZnO). This in turn causes the ethanol to react with the ionic oxygen species that are present in the sensing material which leads to the release of the trapped electrons into the metal oxide. Finally, it reverts back to the space charge region on the surface of the metal oxide. **Figure 12** shows the graphical representation VOC sensing mechanism ZnO-based PS sensor; it clearly represents the reduction of ethanol (electron exchange with sensing layer) sensing mechanism of ZnO. The mechanism flow of sensing is expressed as a flow diagram in **Figure 13**.

4. Conclusion

The novel method for sensing of VOCs using a porous silicon sensor coated with a layer of ZnO has been presented. The key structural aspects have been explained in detail. The coating of ZnO over PS by EPD technique was carried out successfully. The XRD spectrography was used to successfully obtain distinct intensity peaks of 101 and 400 for ZnO and porous silicon which were found at 32.90 and 69.8, respectively. The resistance changes, which varied from 8 to 16 MΩ for methanol, 12 to 15.6 MΩ for isopropanol, and 12 to 15.8 MΩ for ethanol, were observed and studied carefully. This proved that device exhibited higher sensitivity and selectivity at the temperature range between 70 and 250°C for PS sensor coated with ZnO nanoparticles. We also concluded that the device works best for the sensing of ethanol as it showed high repeatability of up to 80% at saturated levels and has high selectivity of about 90% for methanol.

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