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Research Paper

Fabrication of SnO_2 doped TiO_2 Metal Oxide Sensor with Ppy layer to sense CO_2 Gas

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Abstract— In this study, an optically flat glass plate was used in the development of a thick film sensor that was based on an Al_2O_3 substrate that was finer and more porous. The XRD pattern for the B3 sensor seems to point towards a rather tiny crystalline size.. SEM analysis was used to identify the B3 sensor's increased porosity. As the CO_2 gas concentration rises, the sensor resistance reduces at room temperature, enhancing sensitivity because surface oxygen vacancies on TiO_2 and SnO_2 function as donors. The sensor on an $80SnO_2$:$20TiO_2$ composition with PPy as the roofing layer showed the maximum sensitivity among the constructed sensors, 0.5912 at 250 ppm, whereas it is less for other compositions.

Keywords *— SnO_2, TiO_2, Al_2O_3, Sensitivity, Thick Film, Nanocomposites.*

1. Introduction

For the identification of target molecules, it is necessary to distinguish between of "volatile organic compounds, real-time security warnings, and clinical diagnostics, practical applications" need gas sensors with an exceptionally high level of sensitivity and selectivity. Semiconducting tin oxide (SnO_2) is held in very high esteem as a candidate for use as a gas-sensing material on account of its extraordinary reactivity to changes in gaseous environments as well as its great chemical stability [1]. One of the most popular sensors for detecting gases is the metal oxide sensor, which has a high level of stability, good selectivity, and other properties. The sensing procedure for SnO_2 sensors is described in this work, along with a survey and analysis of the several techniques used in order to enhance the gas detection capabilities of SnO_2-based sensors by doping, dynamic responsiveness, and sensor array improvements. It is possible that the composite sensor will significantly increase the gas sensor's ability to detect hazardous and potentially toxic gases. [2].

Polypyrrole (PPy) is a developing intelligent material with several uses in optical, electrical, and electrochromic devices and sensors. In recent years, PPy has emerged as a particularly effective alternative for detecting volatile organic compounds (VOCs), thanks to its selectivity and sensitivity towards target gas molecules. This has made it a very popular choice in this area. In order to construct better sensing devices, work has been done to develop PPy-based sensors with reliable mechanical and electrochemical performance. The goal of this work is to design better sensors. [3]. Because air includes a variety of poisonous chemicals that are dangerous to human health, gas sensors have drawn interest in academic domains and industrial settings [4]. The harmful gases may result in "asthma, skin burning, nausea, vomiting, sleepiness, cancer, lung problems, weight loss, etc". [5].

SnO_2, TiO_2, ZnO, In_2O_3, and WO_3 all have benefits in terms of stability. Scientists have studied various SnO_2 mechanisms, formations, and fundamental characteristics for many years. SnO_2 is the most crucial component for semiconductor sensors in terms of both application and fundamental research. However, low-concentration biogas and odors cannot be detected with SnO_2 thick film for gas alarms [6]. The preparation conditions, dopant, and grain size of SnO_2-based materials, which have a substantial impact on their chemical and physical qualities, are well understood to affect their sensing capabilities. In the presence of humidity, the DC-electrical resistance of SnO_2 doped with TiO_2 sensors was investigated, and SnO_2 and TiO_2 doped with Al_2O_3 were proven effective humidity-detecting materials. The fundamental goal of this study is to build a CO_2 gas sensor in a multi-layer design using a layer of polypyrrole and SnO_2-doped TiO_2. Tin dioxide (SnO_2)-based chemiresistors have a faster gas sensing response than conducting polymer-based chemiresistors, however, they must be used at high temperatures (>200 °C).

2. Related Work

Because of its adjustable electrical, optical, and electrochemical properties during the material fabrication and control of parameters like film thickness, synthesising temperature, synthesising chemicals, acidity level, annealing temperature, and other factors, SnO_2 and TiO_2 thin films have found numerous applications as semiconducting materials [7]. A new type of CO_2 gas sensor was developed by Masayuki et al [8] using porous hydroxyapalite ceramics, both DC and AC conductivities measurement were ca1Tied out in various atmospheres including air, CO_2 and air containing different amount of CO_2. The sensitivity of SnO_2 and TiO_2 thin films was also seen to rise as the film temperature was raised. The above research was combined with an examination of the sensitivity of the obtained SnO_2 doped TiO_2 thin film semiconducting material.

3. Material and Method

3.1 Synthesis of SnO_2 Nanoparticles

In order to carry out the experiment described above, GR-grade chemicals with a purity level of 99.99% were purchased from Sd-fine in India. In order to produce stannous dioxide (SnO_2), 2 grammes (0.1 millimetres) of stannous chloride dehydrate ($SnCl_2.2H_2O$) were dissolved in 100 millilitres of water. After the aqueous solution that was previously used had finished dissolving entirely, 4 cc of an ammonia solution was added while magnetic stirring was performed. A time period of spinning for twenty-five minutes led to the beginning of the formation of a white gel precipitate. After that, it was allowed to rest for ten to fourteen hours before being examined again. After that, it was cleansed in deionized water after passing through four or five filters in the previous process. A total of 0.27 grammes of charcoal-activated carbon black powder was added to the precipitate that was produced as a consequence. After about one day of being ground into powder in a vacuum oven at a temperature of 80 degrees Celsius, the mixer was removed. The dry material was broken up into smaller pieces and then milled into a powder. In order to purge impurities from the end product, the ultrafine SnO_2 nanopowder was calcined in an auto-controlled muffle furnace at a temperature of 700 degrees Celsius for up to seven hours [9].

3.2 Synthesis of TiO_2 Nanoparticles

Iso-propanol [$(CH_3)2CHOH$] and nitric acid [HNO_3] were both utilised straight from their respective containers when they were prepared. Titanium tetra iso propoxide [$Ti(OCH(CH_3)_2]_4$. To a solution that was 22 millilitres in size, drop by drop additions of 20 millilitres of titanium tetra isopropoxide, 10 millilitres of isopropanol, and 12 millilitres of deionized water were made while the temperature was maintained at 80 degrees Celsius. After an hour, 0.80 millilitres of highly concentrated HNO_3 and 0.8 millilitres of deionized water were added to the TTIP solution. After six hours of continuous stirring at 60 ^oC, a very viscous sol-gel was created. Two hours at 300 ^oC were spent heating the prepared sol-gel outside. After annealing, 2g of TiO_2 nanocrystalline powder was created. The produced powder was mixed with the iso-propanol solution in a 1:10 ratio. To acquire thoroughly dried powder, the obtained powder was stored in a vacuum oven at 70 ^oC for 24 hours.

3.3 Synthesis of Polypyrrole

In order to generate the PPy sample, we employed methanol, pure iron (III) chloride ($FeCl_3$), and Py monomer as our ingredients [10]. In a flask with a round bottom, 1.892 grammes of finely powdered $FeCl_3$ and 7 millilitres of a solution containing methanol were mixed together. Following the addition of 8.4 ml of Py monomer, the solution consisting of $FeCl_3$ and methanol was rapidly mixed while being kept in the dark. We were able to predict the maximum yield by utilising the quantity of Py monomer that was added to the solution, which was equal to 1/2.33 times the amount of $FeCl_3$. The resultant dark precipitates were filtered, and then distilled water was used to completely wash them until they were clean and visible. Baking the finished product, or PPy, for three hours at 500 ^oC powdered it.

3.4 Preparations of thick films

The obtained samples were used for screen printing, which resulted in the creation of thick films. Sintered fine powders of pure and composite nano-powders of SnO_2 and TiO_2 in different weight ratios were first mixed with ethyl cellulose as a temporary binder in order to form the thixotropic paste for screen printing. This paste was then used to print on screens. In order to get the desired results, this solution is combined with organic solvents such as terpineol, butyl cellulose, and butyl carbitol acetate. The production of the paste consisted of inorganic chemicals 75 percent of the time and organic ingredients 25 percent of the time. Screen printing was used to apply thick sheets of pure and composite SnO_2 and TiO_2 materials formed from the paste onto a clean glass substrate. Al_2O_3 served as the base for the printing process, as shown in Figure 1.

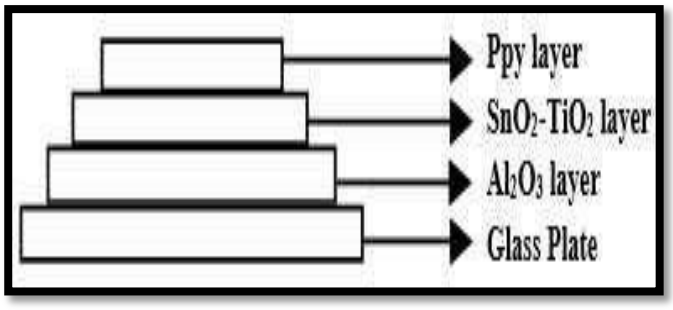


Fig. 1. Sensor with PPy layer

The created films were baked for an hour at 90–100 ^oC to completely evaportate all of the organic materials (in the form of binders) and organic pollutants. Electrodes are made to measure surface conductivity on the thick film's opposing sides, and the silver paint is then dried by heating the film at 70 ^oC for 0.5 hours. The table below displays the samples in order.

Table 1: Sample Codes

Sr. No.	Nanocomposites	Sample Code
1	Pure SnO_2	B1
2	90% SnO_2 + 10% TiO_2	B2
3	80% SnO_2 + 20% TiO_2	B3
4	70% SnO_2 + 30% TiO_2	B4
5	60% SnO_2 + 40% TiO_2	B5
6	Pure TiO_2	B6

4. Result & Discussion

4.1 X-ray Diffraction Study

Figure 2 presents the X-ray diffraction pattern of PPy for your viewing pleasure. The amorphous nature of PPy's structure was shown by XRD. The wide peak was at 26^o and exhibited the amorphous properties of polypyrrole. This large peak is a result of polymer chains scattering X-rays at the inter-planer gap. The monomer-to-oxidant ratio affects the amorphous peak's intensity location.

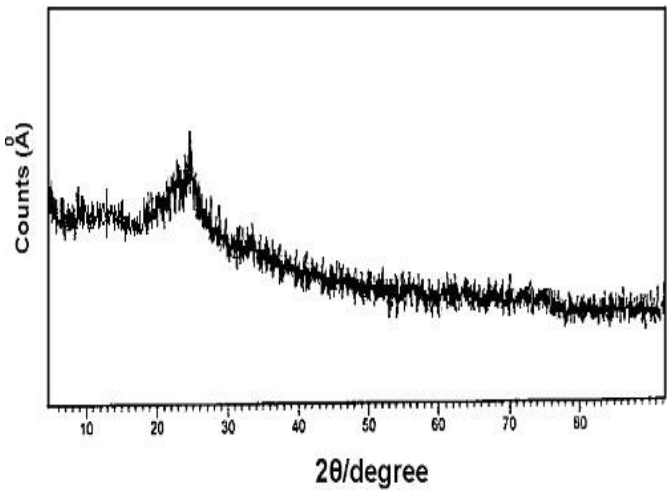


Fig. 2 Polypyrrole's XRD spectra

Fig. 3 shows the pure SnO_2 and TiO_2 X-ray diffraction patterns and composites of SnO_2 and TiO_2 calcinated at 800 ^{0}C for 4-5 h. It is recorded in terms of 2θ in the range 10-100^0. TiO_2 was added in the stichometry of SnO_2 to see whether the sensitivity increases due to addition or not. Prominent peaks of SnO_2 and TiO_2 are observed. It was discovered that the associated peak's intensity rose and peaked for $80SnO_2$:$20TiO_2$ composition. All planes corresponding to the Anatase-tetragonal phase of TiO_2 with space group number 141 [11, 12] are formed. The unit cell parameters a=b= 3.7830, c = 9.5100, $\alpha = \beta = \gamma = 90^0$. FWHM was used to compute the "crystallite size (D)" from Scherer's formula and at least 98.40 nm were discovered for $80SnO_2$:$20TiO_2$ composition and for SnO_2, it was 121.63 nm.

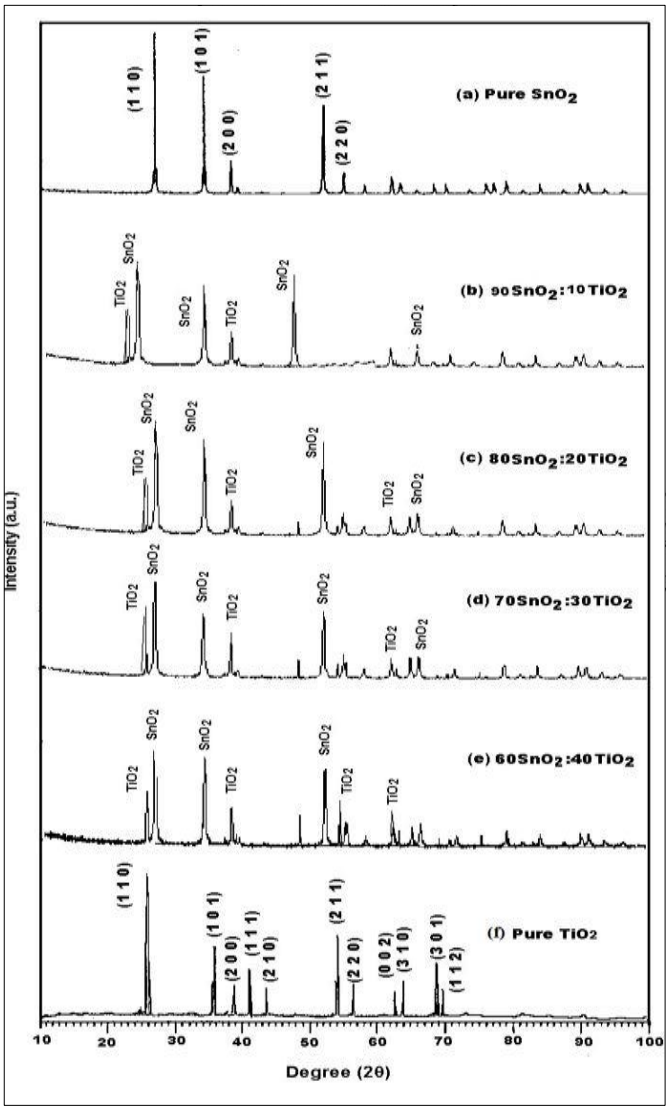


Fig. 3. XRD pattern of SnO_2 -TiO_2 System

Table 2: Average crystallite size of SnO_2, TiO_2 and their compositions

Chemical composition SnO_2:TiO_2 (mole %)	Maximum Intensity Peak Position (2θ) degree	FWHM (2θ) degree	Average Crystallite Size (D) in nm
SnO_2	26.6122	0.1334	121.63
$90SnO_2$:10 TiO_2	26.7158	0.2175	121.57
$80SnO_2$:20 TiO_2	26.6574	0.2175	98.40
$70SnO_2$:30 TiO_2	26.6455	0.2040	148.02
$60SnO_2$:40 TiO_2	26.5674	0.2867	141.04
TiO_2	27.3654	0.27341	132.14

From Table 2, it was observed that average crystallite size of $80SnO_2$:$20TiO_2$ composition is least as compared to other compositions and pure materials and hence $80SnO_2$:$20TiO_2$ composition has large active surface area for sensing the gas.

4.2 SEM study - "Scanning Electron Microscope"

The SEM images (Fig. 4-6) showed that the number of pores varied in every square inch of the region, and hence to compare, an average number of pores was used. For an area of one inch on each shot, porosity was determined.

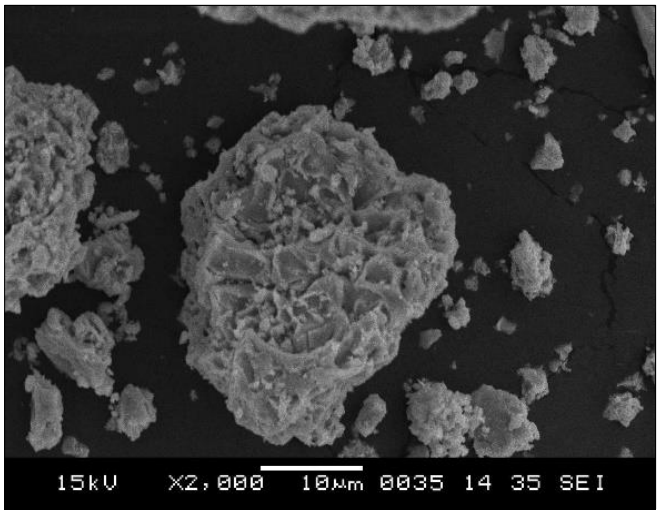


Fig. 4. SEM picture of SnO_2

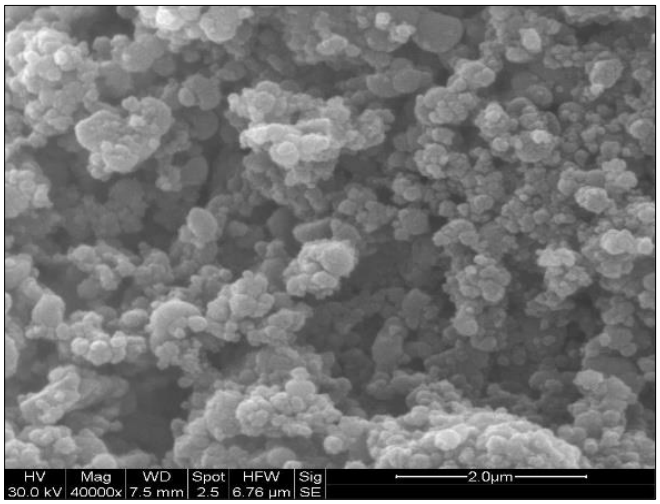
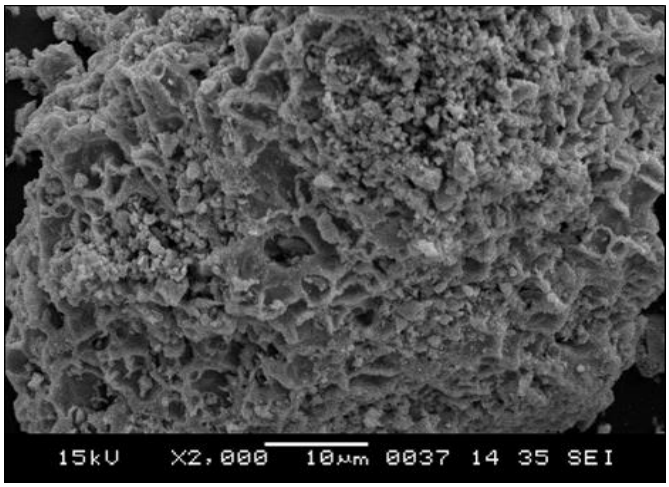


Fig. 5 SEM picture of TiO_2

According to SEM images, the prepared and pure samples had greater porosity than the other samples. High porosity causes an increase in gas absorption or gas sensing. It was found that the lower SnO_2:TiO_2 layers absorb the leftover CO_2 gas when the PPy layer is on the roof of the sensor. Additionally, it was demonstrated that PPy had greater sensitivity when mounted on the B3 sensor.



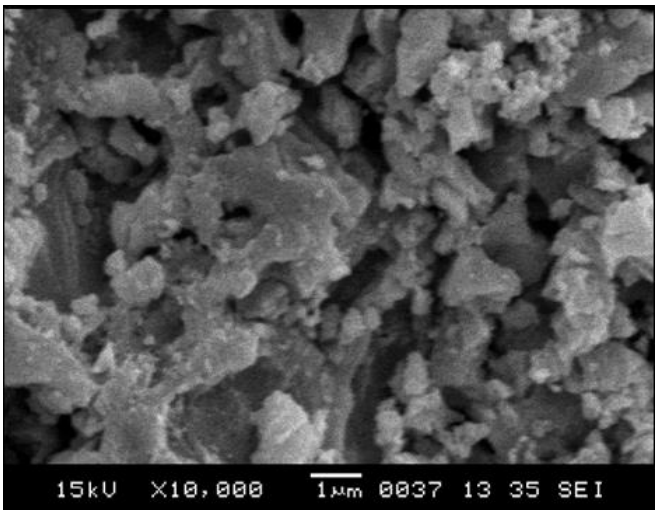


Fig. 6 SEM pictures of $80SnO_2$:$20TiO_2$ at different magnifications

Table 3: average diameters of pore and number of pores per inch of pure samples and their compositions

Pure sample and their compositions (mole %)	**Average diameter of pore (nm)**	**Number of pores per inch (in x 2000 magnification)**
SnO_2	590	67
TiO_2	630	85
$90SnO_2$:$10TiO_2$	390	99
$80SnO_2$:$20TiO_2$	210	132
$70SnO_2$:$30TiO_2$	230	125
$60SnO_2$:$40TiO_2$	250	115

Above table shows the average diameter and number of pores per inch of SnO_2, TiO_2 and composites of SnO_2 and TiO_2. From the SEM pictures, it is observed that $80SnO_2$:$20TiO_2$ composition has more pores per inch (calculated for x 2,000 magnification for each composition) than other compositions of SnO_2 and TiO_2. Thus $80SnO_2$:$20TiO_2$ composition has more surface area and exhibit more sensing nature. It is also found that average diameter of pore in case of $80SnO_2$:$20TiO_2$ composition is small as compared to other compositions. This also tends to exhibit large surface area and high response of the sample.

4.3 Sensitivity

It was shown that sensitivity increases linearly up to 250 ppm for all compositions before reaching saturation. According to Fig. 7, sensitivity rises linearly up to 250 ppm and then reaches saturation. Additionally, it was shown that among the produced sensors, the sensor with "PPy as the rooftop layer on an $80SnO_2$:$20TiO_2$" composition has the maximum sensitivity, 0.5912 at 250 ppm, whereas for other compositions, it is less.

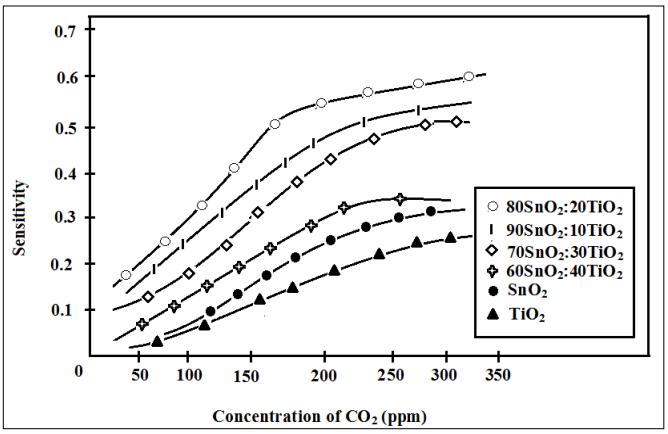


Fig. 7 Sensitivity of the SnO_2:TiO_2 system changes as CO_2 concentration (ppm) increases at RT (303 K).

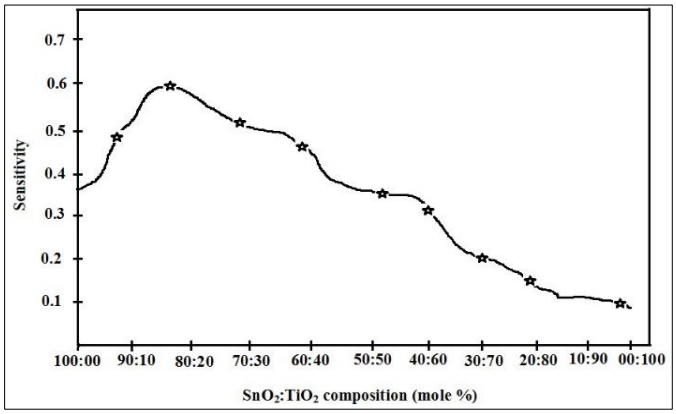


Fig. 8 Variation of sensitivity with SnO_2:TiO_2 (mole %) at 250 ppm of CO_2 gas at 303 K.

From Fig. 8, it was observed that with increase in doping of TiO_2 in SnO_2:TiO_2 composition, sensitivity increases and becomes maximum for $80SnO_2$: $20TiO_2$ composition. With further addition of TiO_2, sensitivity decreases. From SEM picture (table 3), it is found that porosity of $80SnO_2$: $20TiO_2$ composition is large as compared to other compositions of SnO_2 and TiO_2, thus active surface area is more. Also the average crystallite size of $80SnO_2$: $20TiO_2$ composition is small and it means large active surface area. Hence sensitivity of $80SnO_2$:$20TiO_2$ composition is large as compared to other compositions and pure samples.

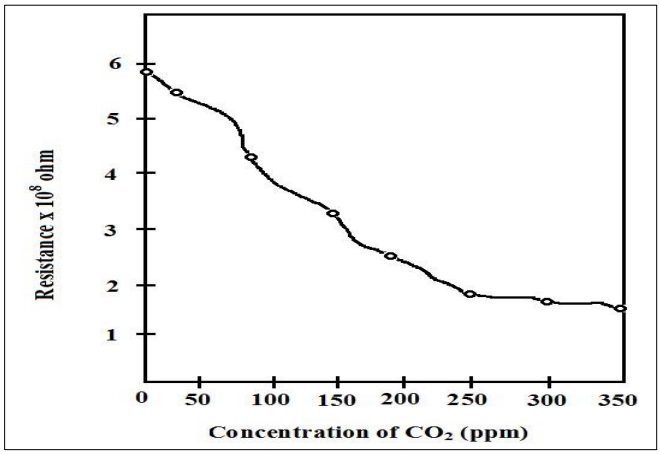


Fig. 9 Variation of resistance of $80SnO_2$: $20TiO_2$ system with CO_2 gas concentration (ppm) at room temperature (303 K).

From the above figure it was perceived that, resistance of $80SnO_2$: $20TiO_2$ sensor decreases with increase in CO_2 gas concentration upto 250 ppm and then becomes nearly constant. Resistance of the sensor is of the order of 100 MΩ at 250 ppm of CO_2. It was found that resistance falls at the rate of 1.7 MΩ per ppm concentration of CO_2 gas.

5. Conclusion

The main aim was to fabricate sensor devise using SnO_2 and TiO_2 materials to improve sensitivity. With this purpose, Al_2O_3 based SnO_2:TiO_2 composite sensors were fabricated by screen printing technique. Series SnO_2:TiO_2 was prepared by different mole percentage and optimize sample was determined. These sensors were used to sense the CO_2 gas at different concentrations and at room temperature. Sensors so fabricated were characterized through XRD and SEM analysis. XRD pattern of SnO_2 and its composite with TiO_2 showed crystalline nature. XRD pattern also showed that crystallite site of $80SnO_2$:$20TiO_2$ is small and hence surface area is more. This indicated the more sensing nature of $80SnO_2$:$20TiO_2$. SEM analysis is used to study the surface morphology of the prepared samples. By considering same magnification, numbers of pores per inch for each composition were determined and from that more surface area was decided. It was found that porosity was more for $80SnO_2$:$20TiO_2$ sample.

The prepared samples were pasted on glass plate in multilayer structure. Al_2O_3 was used as the substrate of the sensor. Interdigited electrodes were used for connection of the sensors. The resistance of the sensor was measured by voltage drop method and it was found that resistance of the sensor decreases with increase of CO_2 gas concentration and sensitivity increases. All the sensors showed saturation at about 250 ppm concentration of CO_2 gas. It was found that $80SnO_2$:$20TiO_2$ sensor showed optimization. The sensitivity of the sensors was measured at room temperature (303 K). The tetragonal structure of composites of SnO_2 and TiO_2 as well as pure SnO_2 and TiO_2 was revealed by the patterns of X-ray diffraction, and it was found that the crystalline size for an $80SnO_2$:$20TiO_2$ composition was at least 98.40 nm. Among the tested sensors, the PPy rooftop layer B3 sensor exhibited the greatest sensitivity, measuring 0.5912 at even very low CO_2 gas concentrations, such as 250 ppm. The high porosity, tiny crystalline size and therefore increased surface area caused this high sensitivity, which demonstrated a stronger reactivity to CO_2 gas. Further, there is a scope to study static and dynamic response of the prepared sensor.

Data Availability

The raw data required for ongoing study, hence it cannot be shared.

Conflict of Interest

Authors declare that they do not have any conflict of interest.

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Authors' Contributions
Experimental, conceptional study, data collection: Mr. B. H. Bhatti; Analysis & interpretation of results : Mr. B. H. Bhatti, Dr. K. B. Raulkar; Draft manuscript design : Mr. B. H. Bhatti; Supervising & editing manuscript : Dr.K. B. Raulkar, Dr. G. T. Lamdhade;

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