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Research Article

Characterization and Gas Sensing Application of Tin Oxide

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Abstract

This paper demonstrates the gas and humidity sensing mechanism of the sensor that is fabricated using tin oxide. The as-synthesized SnO2 structural and morphological characterizations were carried out. Further, it has been mixed with PEG and a thin layer of the paste was applied on FTO glass. For Ethanol (CH3CH2OH), Ammonia (NH3), and Acetone (C3H6O), the output of the gas sensor was tested over a concentration range of 50-500 ppm and a temperature range of 50ºC-250ºC. The experimental results revealed that the SnO2 gas sensor has less sensitivity towards ammonia and more sensitivity towards acetone. The prepared sensor shows excellent response for measuring relative humidity in the range 5-95% at room temperature..

Keywords: nano-materials, gas sensing, sensitivity, humidity, concentration

1. Introduction

In physical, chemical and biological systems, gas sensors have gained immense popularity as it is used to detect, discriminate or monitor the variations in the ambient gas atmosphere. For detection of gas, choice of sensing material for a particular gas is very important. Different parameters such as band-gap, electro-conductivity and catalytic activity are to be considered. Metal oxide semiconductor gas sensors have become a popular option among researchers for gas sensors. The most important factor for increasing the sensitivity and selectivity of nano-materials, which can then detect chemical and biological species (gases) to a greater degree, is a high surface to volume ratio and small scale. SnO_2, ZnO, In_2O_3, WO_3, Fe_2O_3 are widely used metal oxide semiconductors for gas sensing [1-5]. Among these SnO_2 is considered as a good material for detection of gases because of its low cost, strong oxidizing power, good chemical inertness, unique optical property and nontoxic with good response for various gases. SnO_2 is a wide band gap semiconductor material having 3.6eV band-gap energy [6, 7]. The principle for gas detection of SnO_2 gas sensor is based on the resistance variation (or conductance) of the sensing layer with adsorption of gas. Chemical catalytic reactions at the particle surface trigger resistance differences by removing e^-s from the conduction band at high temperatures, creating a space charge layer between conduction band particle surfaces (i.e. modulation of conduction barriers between the oxide particles). Reduced gases, such as CO, oxidise on the surface and absorb the adsorbed oxygen, releasing electrons into the conduction band. As a result, the degradation layer shrinks, lowering the overall film resistance [8]. Tin oxide gas sensors are commonly used to detect both reducing and oxidising hazardous gases. These gases may include methane, carbon monoxide, hydrogen sulfide, ammonia, acetone, nitrogen dioxide etc. under different temperature range [9-11]. Ammonia is the colorless harmful and toxic gas having unpleasant odor. It is dangerous for human health both in the form of natural or industrial emissions. In low concentration it can cause many problems like eye irritation. When concentration is high it may cause lung disease or blindness may be caused. In paper [12], Pd-rGO based gas sensor has been prepared for NO_2 gas sensing. The prepared gas sensor is miniature in size and can work in microwatt range. NiO gas sensor shows good response to

acetone [16] in the given humidity. Structural and morphological characterization of SnO_2 using precipitation method shows porosity for gas Ethanol gas sensing using various nano-materials has been discussed in [18, 19].

2. Fabrication of SnO2 Gas Sensor

The synthesis of SnO_2 nano-powder was carried out by chemical co-precipitation method. To achieve a homogeneous solution, 0.27 M $SnCl_2.H_2O$ was added to double distilled water and ethanol in a 1L beaker and stirred with a magnetic stirrer for 60 minutes. To minimize the precursor, HCl was added drop wise, and the solution was stirred for 30 minutes to ensure proper mixing, resulting in a transparent solution. After that, aqueous ammonia was mixed in drops till the pH value was reached to 7.5-9.0, resulting in a milky white solution. For another 3 hours, the solution was continuously stirred. After that, the stirring was turned off and the beaker was left alone overnight to allow the particles to settle fully. The dried powder was annealed at 400 °C to get a white powdered tin oxide [10]. Fluorine doped tin oxide (FTO) coated glass having surface resistance of 8Ω/sq. was purchased from Sigma Aldrich and then cleaned by using double distilled water. It was kept in acetone for sonication for 6 hours. The SnO_2 nanomaterial was mixed with ethanol and Poly ethylene glycol (which acts as a binder) and then grounded by using motor pestle for 30 minutes. The paste was then applied on the finger electrode FTO glass using doctor blade method. The films were kept in the furnace for 30 minutes at 300^{o}C for drying.

3. Characterization Techniques

X-Ray Diffraction (XRD) was used to examine the nano-material's crystalline structure as shown fig.1. According to JCPDS data 41-1445, the reported XRD pattern confirms to the tetragonal structure of SnO_2.

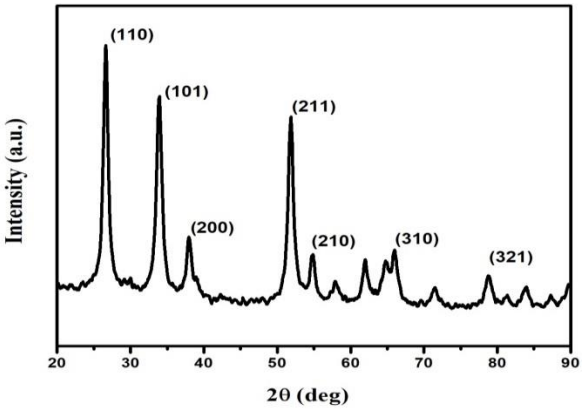

Fig.1. X-Ray Diffraction of SnO_2

Major peak positions can also be seen at 26.59, 33.89, and 51.79 degrees, which corresponds to d-spacing of 3.34, 2.64, and 1.76, that consider interplanar spacing with miller indices of 1 1 0, 1 0 1, and 2 1 1 and FWHM of 0.7, 0.81, and 0.77 degrees. The Scherrer's method can be used to approximate the crystallite size 'D' of SnO_2 nanomaterial (equation 1)[16].

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where k=0.9 is the form factor , λ= 1.54059 Å for Cu-kα radiation, 'β' is the full width at half maxima peak , and 'θ' represents Bragg's angle. The mean crystallite size of SnO2 nanomaterial has been calculated to be 11.8 nm. The non-appearance of projecting peaks over the common peaks indicates that the prepared nanomaterial is single phase and impurity-free.

Surface Electron Microscopy (SEM) reveals that the particles are almost circular in shape, with some patchy rod-like features and clusters (Fig. 2). Also, it confirms that the prepared sample has an average crystallite size of 11.8 nm.

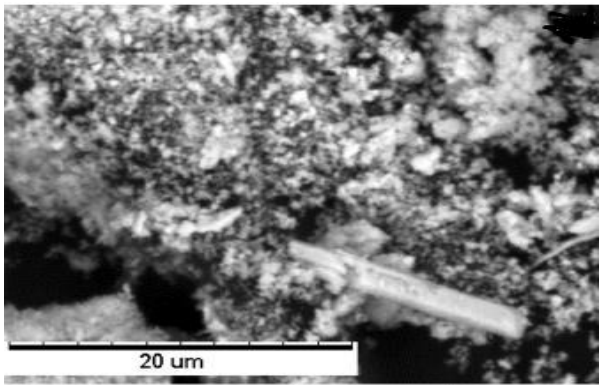

Fig.2. SEM of SnO_2

The elemental morphology of the specimen was measured by using EDX as shown in fig. 3. The majority of Sn and O peaks exist in the required proportion, demonstrating the creation of SnO_2 nano-materials, according to the research. There are also some peaks of C and Al, which exists due to the tape which was used to disseminate the sample.

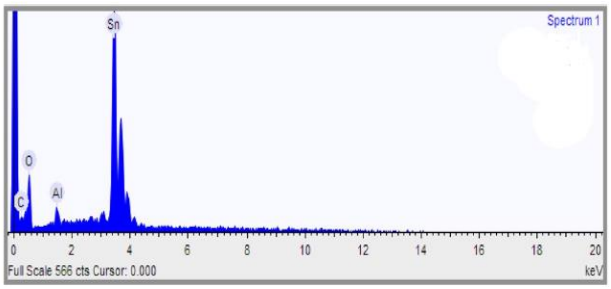

Fig.3. EDX of SnO_2

To validate with the functional groups and verification of the production of SnO_2, an FTIR analysis of the SnO2 nano-material was performed in the wavelength range 400–4000 cm^{-1} as shown in fig.4. The production of SnO_2 is indicated by the large peaks between 500 and 700 cm^{-1}[20, 21]. The presence of ethanol causes the remaining peaks corresponding to carbonyl and hydroxyl groups, further confirming the purity of the prepared nanomaterial.

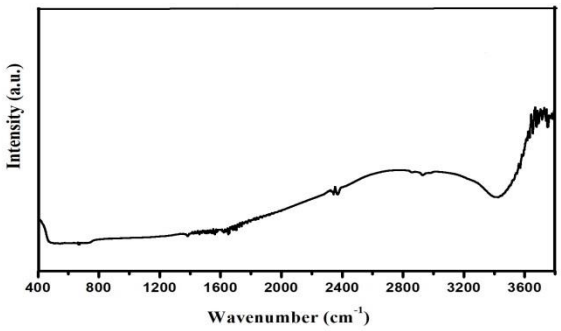

Fig.4. FTIR of SnO_2

4. Gas Sensing Characterization

The performance of the gas sensor was investigated inside the gas sensing unit. The baseline resistance was noted at the room temperature. After that, 200 ppm ammonia was injected into the chamber through a flow meter, and the resistance was calculated at a specific temperature until saturation was detected, after which the sensor was exposed to fresh air for recovery. At 50, 100, 150, 200, and 250 degrees Celsius, the sensor's resistance was measured. Similarly for ethanol and acetone the baseline resistance was measured in air and at different temperatures by the same method used for ammonia. The response of the gas sensor is given by [11]

$$\frac{(Rg-Ra)}{Ra} \qquad (2)$$

In equation 2, "R_g" stands for sensor resistance when exposed to gas, while "R_a" represents sensor resistance when held in air.

The gas response of sensors is considerably affected by operating temperature. The gas response characteristics of the tin oxide w.r.t. operating temp. in the span of 50º C to 250º C at 200 ppm with various gases are shown in fig.5.

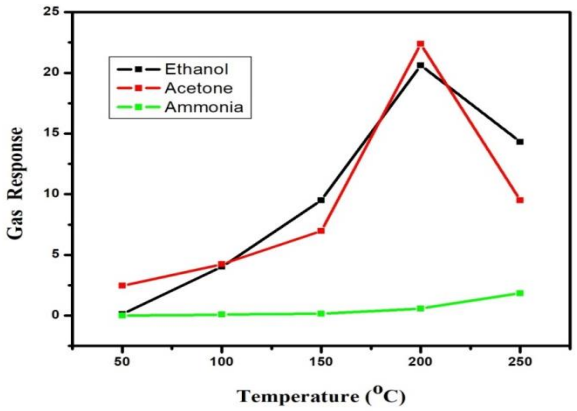

Fig.5. Response of sensor at different temperatures

While SnO_2 did not display any substantial sensitivity to ammonia, it has the potential to be used as a sensing material for acetone and ethanol detection. The response of SnO_2 gas sensor first increases and reach the highest value and then decrease with respect to operating temperature. The quantity of gas molecules accumulation reaches equilibrium at the pertinent temperature. This equilibrium is disrupted above this temperature and the gas response decreases. The dynamics and kinetics of gas adsorption and desorption on SnO_2 surfaces are well-known in this regard [14, 15]. The accumulation of gas molecules moderately raise on the surface with the rise in temperature till equilibrium is achieved. If the temperature is further increased, the balance will change to absorption, as it is an exothermic reaction, hence the gas response will decrease. The SnO_2 sensor gives maximum response for acetone and minimum for ammonia, as shown in fig 5. It shows the comparison of response of the gas sensor towards different gases with the temperature range 50-250ºC. Fig.6 shows that it gives optimum response at 200 ºC. From the fig.7 it can be noticed that the response of the sensor rises with the rise in gas concentration for both for acetone and ethanol. However, the increment is fast in case of acetone while there is gradual rise in case of ethanol.

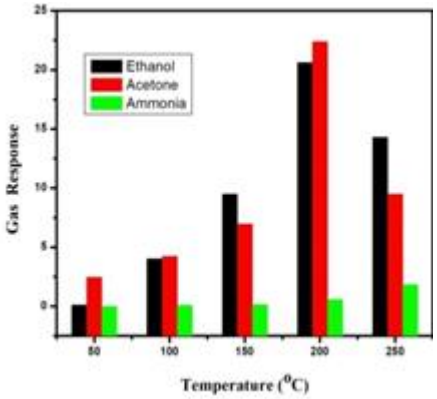

Fig.6. Histogram of Response versus Temperature

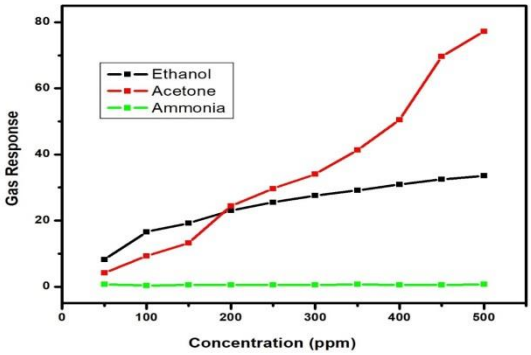

Fig.7. Response of sensor at different gas concentrations

The humidity sensing experiment is carried out in a chamber along with water in a beaker. The humidity of the sensor was measured using a hygrometer. The observations were made at room temperature in order to allow for associative adsorption. Fig.8 shows the characteristic of sensitivity with change in relative humidity. The decrease in DC resistance or significant increase in conductivity with the increase in relative humidity was observed.

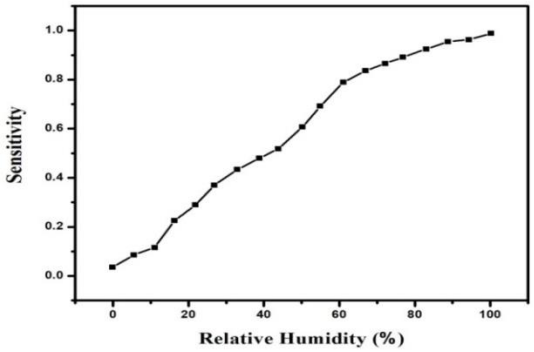

Fig.4. Change of sensitivity with relative humidity (%).

This action took place because of the free electrons in water molecules. The conductivity (G=1/R) of SnO_2 gets affected by this phenomenon. The change in resistance versus relative humidity is shown in fig.9.

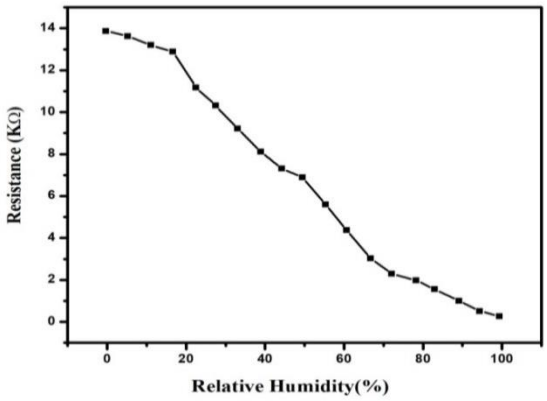

Fig.9. Change of resistance (kΩ) with relative humidity (%)

The sensitivity is defined as $(G_{DA}-G_{MA})/ G_{MA}$ where G_{MA} is the conductivity of moisture air and G_{DA} is the conductivity of dry air. The variation shows good sensing and linearity with relative humidity. At high temperature (100^0 C and above), water molecules can react with Sn and O on the surface and release electrons.

5. Conclusion

In this paper, XRD and SEM confirm that the prepared nanomaterial has an average crystallite size of 11.8 nm. Also EDX confirms that prepared sample is SnO_2 and impurity free which was further confirmed by FTIR. It has been confirmed that the as-synthesized tin oxide can be used as a gas sensor due to its small particle size

and unavailability of any impurity. The low cost, highly sensitive gas sensor and humidity sensor has been demonstrated. The sensor is highly selective. It gives good response to acetone gas as compared to other gases. This makes the sensor to be used in medical for disease diagnoses in exhaled breathe analysis. Also, the prepared sensor shows excellent response for measuring relative humidity in the range 5-95% at room temperature. Moreover, this simple, cost effective sensor shows excellent applications in environmental monitoring and humidity controlled device.

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