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Investigating the Semiconductor Gas Sensor to Detect $SO_2$with Substrate Pure SnO_2, V_2O_5 and SnO_2:V_2O_5 Composite

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ABSTRACT

Detection of toxic gases like carbon monoxide, nitrogen oxide, methane and sulphur dioxide is extremely important, since they have destructive effects on human health. The detection of one such gas pollutant, namely sulphur dioxide is of much importance because this gas forms the exhaust of most of the sugar industries; since the burning of bagasse in fuel boilers emit such hazardous gases, and also the sulphination process of sugar involves emission of SO_2. In woolen or cloth industries, SO_2 acts as a mild bleaching agent, hence is widely used. SO_2 is reported to be extremely toxic to humans especially to the respiratory system, eyes and skin. Hence there is an increasing requirement to monitor the gas pollution in urban agglomerates or in the work ambient atmosphere. To this purpose there is immediate need for room temperature, low-cost, sensitive and reliable gas sensors. Semiconductor sensors for detection of toxic gases appeared in market almost 30 years ago, involving materials such as SnO_2, TiO_2, Vanadium oxides, WO_3 and so on. Different physical and chemical deposition method are very well known and are actually used, like reactive sputtering , electron beam deposition, thermal evaporation , sol–gel and spray pyrolysis and many others. In this project we used spray pyrolysis method for synthesize gas sensor. Also we maked three types gas sensors by using SnO_2, V_2O_5 and SnO_2:V_2O_5 composite. Then we tested these sensors by SO_2 gas To Synthesize three types (SnO_2 ,V_2O_5 ,composition of both) gas sensors by using chemical method & get the I-V characteristic from the sensors using graphical representation.

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INTRODUCTION

Nanotechnology (NT) is the production and use of materials at the smallest possible scale100 nanometers or less. One hundred nanometers is approximately 1/800th the width of a human hair and 1/70th the diameter of a red blood cell. Materials at the nano scale often exhibit very different physical, chemical, and biological properties than their normal size counterparts. While we know little about possible adverse effects of nanotechnology, we know enough to recognize that there needs to be some type of governmental oversight to ensure that public health and safety are not adversely affected. Nanotechnology is difficult to address using existing regulations. There are a number of existing laws notably the Toxic Substances Control Act; the Occupational Safety and Health Act; the Food, Drug and Cosmetic Act; and the major environmental laws (Clean Air Act, Clean Water Act, and Resource Conservation and Recovery Act) that provide some legal basis for reviewing and regulating NT materials. However, all of these laws either suffer from major shortcomings of legal authority, or from a gross lack of resources, or both. A new law may be required to manage potential risks of nanotechnology**.** The law would require manufacturers to submit a sustainability plan which would show that the product will not present an unacceptable risk. The political obstacles to passing new legislation are very large, though not impossible, and the drawbacks of trying to fit NT under existing laws make the attempt worthwhile.

1-2- Gas Sensors:

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Gas sensors interact with a gas to initiate the measurement of its concentration. The gas sensor then provides output to a gas instrument to display the measurements. Common gases measured by gas sensors include ammonia, aerosols, arsine, bromine, carbon dioxide, carbon monoxide, chlorine, chlorine dioxide, Diborane, dust, fluorine, germane, halocarbons or refrigerants, hydrocarbons, hydrogen, hydrogen chloride, hydrogen cyanide, hydrogen fluoride, hydrogen selenide, hydrogen sulfide, mercury vapor, nitrogen dioxide, nitrogen oxides, nitric oxide, organic solvents, oxygen, ozone, phosphine, silane, sulfur dioxide, and water vapor.

Important measurement specifications to consider when looking for gas sensors include the response time, the distance, and the flow rate. The response time is the amount of time required from the initial contact with the gas to the sensors processing of the signal. Distance is the maximum distance from the leak or gas source that the sensor can detect gases. The flow rate is the necessary flow rate of air or gas across the gas sensor to produce a signal.

1-3- How we can detect gas:

Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring, and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors, through nanoengineering .Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their use, often in favor of more expensive approaches. Recent advances in nano materials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume. The recent availability of various metal oxide materials in high-surface-area nano powder form, as well as implementation of newly developed nanofabrication techniques, offer tremendous opportunities for sensor manufacturers.

The purpose of the project is to detect small scale gas concentrations in ppm (part per million) and ppb (part per billion) by using nanosensors (sensors used nonmaterial) and give new feature for displaying by using microcontroller. Sensor synthesis using nanoparticle is also very important part of this project. Nanomaterial in thin film form has capability to achieve desired task due to its properties like high surface to volume ratio and small size. Thin film of SnO_2 (Tin Oxide) nano material is prepared by using SPT (Spray Pyrolysis Technique). The type of the gases like CO, SO_2, O_2, and various types of toxic and non toxic gases can be sensed by using metal oxide nanomaterials.

1-4- Methods for synthesize of gas sensor:

Different physical and chemical deposition method are very well known and are actually used, like reactive sputtering , electron beam deposition, thermal evaporation , sol–gel and spray pyrolysis and many others. In this project we used spray pyrolysis method for synthesize gas sensor. Also we maked three types gas sensors by using SnO_2, V_2O_5 and SnO_2:V_2O_5 composite. Then we tested these sensors by SO_2 gas.

2- Semiconductor oxide gas sensor:

Since the semiconductor gas sensors were first reported in 1962, these devices have been subjected to extensive research for detecting small amounts of inflammable, toxic gases in air. Among them SnO_2 based gas sensors were mostly noticed because of their high sensitivity, low cost, fast response speed, and low power consumption. However, there are also some problems in SnO_2-based sensors, of which a serious one is the relative lack of selectivity, since the chemisorbed oxygen (responsible for controlling surface conductivity) reacts with a wide range of reducing gases. Up to date, the most popular methods to obtain stable specificity are the addition of catalysts or doping materials (usual transitional metals) into the pure SnO_2 sensing materials. For example, Bulpitt and coworkers obtained selectivity towards C4 hydrocarbon gases by addition of Pd, and Coles got selectivity to H_2 and CO by the addition of different amount of Bi_2O_3. However, the doping method is a relatively complex preparing process. In this work, we present a new method for synthesizing ethanol sensitive SnO_2 sensing material, which has few been reported to our knowledge. The SnO_2 nanoparticles were prepared by two-steps: solid state reaction, followed by thermal oxidation. We have measured the gas-sensing property of the SnO_2 nanocrystalline, It was discovered decades ago that atoms and molecules interacting with semiconductor surfaces influence surface properties of semiconductors, such as conductivity and surface potential. Semiconductor gas sensors have been widely used as domestic and industrial gas detectors for gas-leak alarm, process control, pollution control, etc.

Compared to the organic (such as phenenthrene, polybenzimidole) and elemental (such as Si, Ge, GaAs, GaP) semiconductors, semiconductor oxides have been more successfully employed as sensing materials for the detection of different gases, such as CO, C O_2, H_2, alcohol, H_2O, NH_3, O_2, NO_x , etc. Both n-type (such as SnO_2, TiO_2 and ZnO) and p-type semiconductor oxides can be used as gas sensor materials. The most widely used semiconductor sensor material is SnO_2. The increases of conductance of SnO_2 caused by the surface reactions

between preadsorbed surface oxygen species and reducing gases are used to detect the concentrations of reducing gases.

Many approaches have been attempted to modify the sensing properties of these semiconductor oxide gas sensors in order to achieve high sensitivities and selectivities. The enhancement of the sensing properties of the sensor materials have been mainly achieved by development of unique preparation methods to fabricate sensors (such as thin-film, thick-film, and sol-gel methods) and the addition of transition metals onto sensors. However, the progresses on this study are still not satisfactory till now.

Tin oxide (SnO_2) is the most widely used semiconductor material for the production of commercial gas sensors.The main reasons for this are its high surface sensitivity to gas adsorption, simplicity and fast response time. Nevertheless, progress in the study of sensor characteristics (gas selectivity, operating temperature, etc.) is still required and there have been numerous recent studies on SnO with the aim of improving knowledge about the surface behaviour and gas-sensitivity mechanism.

One of the existing SnO, gas-sensitivity models is based on the presence of surface defects in the crystalline structure. Oxygen vacancies act as donors and this is reflected in the appearance of a significant density of states in the band gap around the Fermi level. Sensitivity changes can also be induced by doping (i.e., introducing new electron ic states in the SnO, bandgap) or using the catalytic effect of noble metals.

Rutile tin oxide (SnO_2), a wide band gap (3.6 eV at 300 K) *n*-type semiconductor material, is widely used as sensing elements in gas sensors. The sensing mechanism is based on the fact that the adsorption of oxygen on the semiconductor surface can cause a significant change in the electrical resistance of the material.

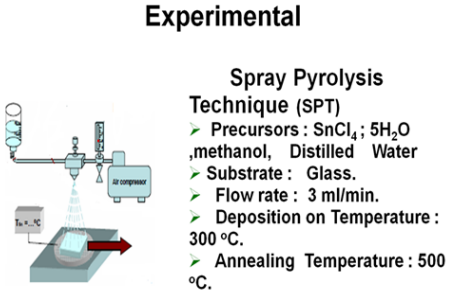
The formation of oxygen adsorbates (O^-_2 or O^-) results in an electron-depletion surface layer due to electron transfer from the oxide surface to oxygen.

Recent studies have shown that the use of tin oxide nanocrystals as sensing elements significantly improves the response and the sensitivity of sensors since the space charge region may develop in the whole crystallite. Tin oxide nanoparticles have been produced by both colloidal and aerosol routes. The colloidal synthesis route affords considerable control over particle size and structure since the surface chemistry can be manipulated through adjustment of the solution properties.

Nanoparticles produced in the gas phase can be subsequently deposited onto solid substrates for immediate device applications. Aerosol routes hence provide more flexibility in process control and improve the compatibility of the nanoparticle sensor fabrication process with existing microelectronics fabrication facilities. In addition, the higher processing temperature employed in aerosol synthesis facilitates production of stable phases that are difficult to achieve in colloidal synthesis.

3-1- Thin film by Spray pyrolysis Technique (SPT):

SnO_2 and V_2O5 thin films were prepared by using Spray pyrolysis technique (SPT) on amorphous glass substrate. Initial amorphous glass substrate were washed by using soap water in ultrasonicator for 15 minuets and after that for 5 minuets by distilled water and 5 minutes by acetone .In this expriment $SnCl_4.5H_2O$(stannic chloride hydrated) , Methanol(CH_3OH) ,distilled water(H_2O) for SnO2(stannous oxide) thin film and V_2O_5(Vanadium pentoxide) ,Citric acid($C_6H_8O_7$) and Distilled water for V_2O_5 thin film were used .



3-2- Synthesis of SnO_2 (tin dioxide) film:

$SnCl_4$ 0.17M dissolved in methanol and distilled water (9:1 ratio) and sprayed on glass substrate at working temperature 300 ^OC with flow rate 3 ml/minute.

3-2-1- Calculation for Molarities for snO_2 sample:

Molecular weight of $SnCL_4.5H_2O$ (stannic chloride hydrated):

Sn $\rightarrow$ 118.710 × 1 = 118.710gm , Cl $\rightarrow$ 35.4527 × 4 = 141.8108 gm

H $\rightarrow$ 1.00794 × 10 = 10.0794 gm , O $\rightarrow$ 15.9994 × 5 =79.997 gm

Total = 350.5972 gm in 1 Litter distilled water $\rightarrow$ 1 M

50 (ml) × 10^{-3} × 0.17 (M) × [350.5972(gm) /1M] = 2.980 gm

2.980 gm ($SnCL_4.5H_2O$) + 50Ml (distilled water & Methanol) $\rightarrow$0.17M
Ratio distilled water (H_2O) & Methanol is 1:9(5 mL D.W & 45mL **3.3**

3-3-Synthesis of V_2O_5 (Vanadium pentoxide) film:

V_2O_5 (12.5mM) in Citric acid ($C_6H_8O_7$) (0.05M) in distilled water (50 ml) is sprayed prepared amorphous glass substrate with 3ml/min. flow rate and 300 ^{0}C working temperature of the substrate in open air environment. Samples were annealed at 500 ^{o}C for 2 hours for phase formation. Then Samples are studied for Room temperature sensing of sulpher dioxide (SO_2).

3-3-1- Calculation for Molarities for V_2O_5 sample:

V $\rightarrow$ 2 × 50.9415 = 101.883 O $\rightarrow$5 × 15.9994 =79.997
Total = 101.883 + 79.997 = 181.88 gm
50 (ml) × 10^{-3} × 12.5 (mM) × [181.88(gm) /1M] = 0.11367 gm
V_2O_5:1M 181.88 gm 1000mL
12.5mM **0.11367 gm** 50mL

Citric Acid:

C$\rightarrow$ 12.011×6 =72.066 H$\rightarrow$ 1.00794×8 =8.06352
O$\rightarrow$ 15.9994×7 =11.9958
Total = 72.066+ 8.06352+11.9958= 192.13 gm
1M 192.13 gm 1000ml
0.05M **0.48032** gm 50ml
50 (ml) × 10^{-3} × 0.0.05 (M) × [192.13(gm) /1M] = 0.48032 gm
Citric Acid (0.48032 gm) + V_2O_5 (0.11367 gm) in to distilled water (50mL)

3-4- Synthesis of V_2O_5: SnO_2 composite bilayer film:

Composite bilayer samples are prepared by over layer spraying of V_2O_5 on SnO2 with same parameters for individual ones and these samples are also anneled at 500 ^{o}C. These samples are then studied for Room temperature sensing of sulpher dioxide (SO_2).These Prepared samples are shown in fig 3.4-1.

Fig. 3.4-1: Prepared Samples.

Fig.3.5-1: Prepared Sensors.

3-5- Room temperature Gas Sensing:

Two contacts were made on samples by using thin copper wire (36 SWG i.e standard wire gate) and silver paste. These prepared samples with contact are shown in fig.3.5-1. Then Samples are placed in spherical shape glass chamber (Volume of chember = 1800 cm^3) and two contacts are removed by boring to glass chamber and

then bores are closed with adeltite. Vacuum is created in chamber and initial resistance of the sample was measured. Dry air resistance of the sample is also measured, SO_2 of required ppm(part per million) is introduced in to chamber by mili and micro syringe and change in resistance is noted with respect to time (for 30 seconds).

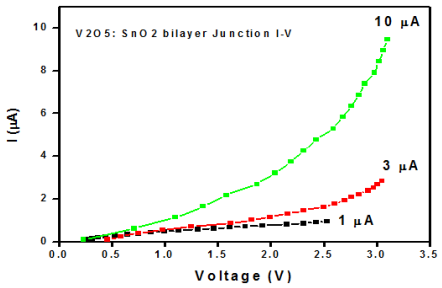


Fig. 4-1: characteristics of Composite (V_2O_5: SnO_2).

4-1- I-V characteristics:

Fig.4-1 Shows I -V characteristics of composite V_2O_5: snO_2 which shows non linear behavior. For taking I-V characteristics of these sensors we used from nanovoltmeter and current source which are shown in fig. 4-2 and 4-3. This non linear behavior is may be due to formation of p-n junction in which SnO_2 act as n type and V_2O_5 act as p type semiconductor. Pure snO_2 and pure V_2O_5 showing linear I-V characteristics individually not shown here. Here we have studied I-V characteristics of composite samples with different current art 1uA,3uAand 10uA respectively in which it is observed that junction resistance of composite system is decreasing with increasing in current thus may be due to high current flowing through the junction .Biasing characteristics of the composite system is also have to study. Non linear behavior plays important role in gas sensing behavior.

Fig. 4-2: Nanovoltmeter.

Figure 4-2, 4-3 and 4-4 shows response to SO_2 reducing Gas with time at room temperature for the time period of 30 seconds for pure SnO_2 ,pure V_2O_5 and composite system respectively. Fig 4-5 is showing sensing behavior of composite system in which it is observed that response and recovery is very fast which could be attributed to fast operated devices and it may also used as real time sensing systems. In the above three observation Pure SnO_2 is showing sensitivity **S= 1.67**,pure V_2O_5 is showing sensitivity **S= 2.16** at room temperature., but recovery of the both pure ones are 8 minute and 3 minutes respectively which could be observed in figures . Figure 4.4.5 shows composite bilayer system, it shows sensitivity **S= 1.33**.When we use composite bilayer system; it shows very fast recovery of just 30 sec. at room temperature. Sensitivity of the samples is calculated by using formula:

S= (Ra-Rg)/Ra

Where

S- Sensitivity

Ra- resistance of sample in dry air i.e. initial resistance.

Rg- resistance of sample in SO_2 gas i.e. final resistance.

5-1- Conclusion:

We can detect some of the gases with special type of substrate and sensing material. In this project we understood for sensing of SO_2 Gas, V_2O_5: SnO_2 composite bilayer film substrate is better than SnO_2 and V_2O_5 thin films.

Fig. 4-3: DC and AC Current Source.

4-2- Sensing characteristics:

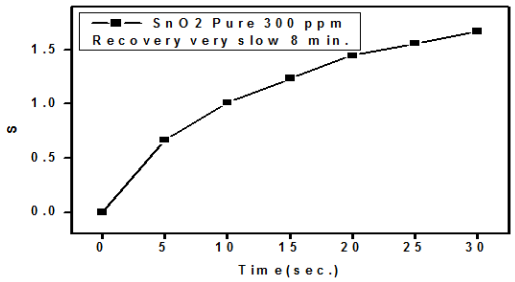


Fig. 4-2: Pure SnO_2.

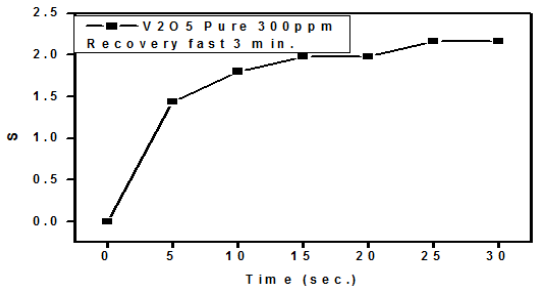


Fig. 4-3: Pure V_2O_5.

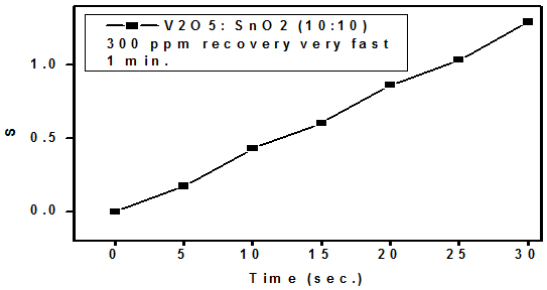


Fig. 4-4: Composite.

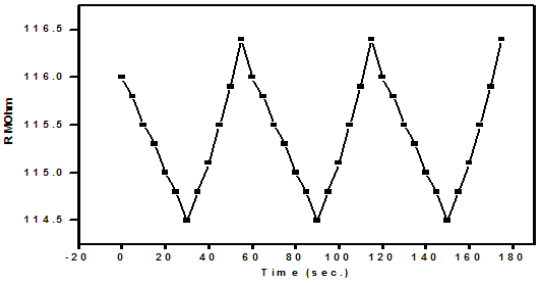


Fig. 4-5: Sensing Behavior.

I -V characteristics of composite V_2O_5: snO_2 which shows non linear behavior. This non linear behavior is may be due to formation of p-n junction in which SnO_2 act as n type and V_2O_5 act as p type semiconductor. Pure snO2 and pure V_2O_5 showing linear I-V characteristics individually not shown here. Here we have studied I-V characteristics of composite samples with different current art 1uA, 3uA and 10uA respectively in which it is observed that junction resistance of composite system is decreasing with increasing in current thus may be due to high current flowing through the junction.

Room temperature gas sensing for time period of 30 seconds is studied for pure SnO_2, pure V_2O_5 and composite system, it is observed that response and recovery of individual sample is very slow where as Composite system shows very fast response and recovery of the order of 30 seconds which could be attributed to fast operated devices and it may also used as real time sensing systems. Sensitivity of Pure samples is better than composite but is not useful for sensing devices.

Fast response and recovery in composite system could be attributed due to band bending of two different systems when comes in contact with each other they are trying to matches their Fermi levels. When Gas is also comes in contact again it will modifies its bands by matching Fermi levels. So this system is not that much stable as individual ones i.e. Pure SnO_2 and Pure V_2O_5. So it always try to comes in stable state so might be showing fast recovery.

It is observed from above experimentation composite systems are act as novel room temperature sensor than individual ones.

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