Gas detection with $\text{V}_2\text{O}_5 : \text{SnO}_2$ composite bilayer film substrate

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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. $\text{SO}_2$, is reported to be extremely toxic to humans especially to the respiratory system, eyes and skin. For this purpose there is immediate need for room temperature, low-cost, sensitive and reliable gas sensors. We can detect some of these gases with special type of substrate and sensing material. Sensor synthesis using nanoparticle is 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. Spray pyrolysis technique was used for creative of $\text{SnO}_2$, $\text{V}_2\text{O}_5$ and $\text{V}_2\text{O}_5 : \text{SnO}_2$ thin films. In this article preparing of different gas sensors with different substrate ($\text{SnO}_2$, $\text{V}_2\text{O}_5$, and $\text{V}_2\text{O}_5 : \text{SnO}_2$ composite bilayer) are tested. Room temperature gas sensing for pure $\text{SnO}_2$, pure $\text{V}_2\text{O}_5$ 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.

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INTRODUCTION

Production and use of materials at the nanometer scale is called nanotechnology (NT).

Materials at the nano scale often exhibit very different physical, chemical, and biological properties than their normal size counterparts.

Gas sensors interact with a gas to initiate the measurement of its concentration. The gas sensor then provide output to a gas instrument to display the measurements. Common gases measured by gas sensors include ammonia, aerosols, arsenic, 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.

The type of the gases like CO, $\text{SO}_2$, $\text{O}_2$, and various types of toxic and non toxic gases can be sensed by using metal oxide nanomaterials. 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 $\text{SO}_2$. In woolen or cloth industries, $\text{SO}_2$ acts as a mild bleaching agent, hence is widely used.

$\text{SO}_2$ 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.

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 nanotechnology. 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).

**METHODOLOGY**

Sensor synthesis using nanoparticle is 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. Tin oxide ($\text{SnO}_2$) 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. Thin film of $\text{SnO}_2$ (Tin Oxide) nanomaterial is prepared by using SPT (Spray Pyrolysis Technique), we can write follow steps as methodology of this project.

**Thin film by spray pyrolysis technique (SPT)**

$\text{SnO}_2$ and $\text{V}_2\text{O}_5$ thin films were prepared by using Spray pyrolysis technique (SPT) on amorphous glass substrate.

(a) **Synthesis of $\text{SnO}_2$ (tin dioxide) film**

$\text{SnCl}_4$ 0.17M dissolved in methanol and distilled water (9:1 ratio) and sprayed on glass substrate at working temperature 300 °C with flow rate 3 ml/minute.

(b) **Synthesis of $\text{V}_2\text{O}_5$ (Vanadium pentoxide) film**

$\text{V}_2\text{O}_5$ (12.5mM) in Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (0.05M) in distilled water (50 ml) is sprayed prepared amorphous glass substrate with 3ml/min. flow rate and 300 °C working temperature of the substrate in open air environment. Samples were annealed at 500 °C for 2 hours for phase formation. Then Samples are studied for Room temperature sensing of sulphur dioxide ($\text{SO}_2$).

**Synthesis of $\text{V}_2\text{O}_5$; $\text{SnO}_2$ composite bilayer film**

Composite bilayer samples are prepared by over layer spraying of $\text{V}_2\text{O}_5$ on $\text{SnO}_2$ with same parameters for individual ones and these samples are also annealed at 500 °C. These samples are then studied for Room temperature sensing of sulphur dioxide ($\text{SO}_2$).

**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. Then Samples are placed in spherical shape glass chamber (Volume of chamber = 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, $\text{SO}_2$ 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).
RESULTS

I-V characteristics

Figure 1 Shows I-V characteristics of composite V_{2}O_{5}:SnO_{2} which shows non linear behavior. For taking I-V characteristics of these sensors we used from nanovoltmeter and current source. It is due to that we have two different thin layers with same n-type conductivity. As can be supposed form the values of resistance form TABLE 1, both SnO\textsubscript{2} and V_{2}O_{5} are partially reduced (the specific resistivity of stoichiometric SnO\textsubscript{2} and V_{2}O_{5} is about 10^{12} \ \Omega \ \text{cm}) therefore they both are certainly n-type semiconductors. Pure SnO\textsubscript{2} and pure V_{2}O_{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. Non linear behavior plays important role in gas sensing behavior.

Dry air resistance of the samples is measured, SO\textsubscript{2} of required ppm (part per million) is introduced into chamber by milli and micro syringe and change in resistance is noted with respect to time (for 30 seconds) for three types samples as follow:

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>R\textsubscript{a}</th>
<th>R\textsubscript{g}</th>
<th>(R\textsubscript{a} - R\textsubscript{g})/ R\textsubscript{a}</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{2}</td>
<td>8.98</td>
<td>8.83</td>
<td>0.01670</td>
<td>1.67</td>
</tr>
<tr>
<td>V_{2}O_{5}</td>
<td>5.54</td>
<td>5.42</td>
<td>0.02166</td>
<td>2.16</td>
</tr>
<tr>
<td>SO\textsubscript{2}:V_{2}O_{5}</td>
<td>116.0</td>
<td>114.45</td>
<td>0.0133</td>
<td>1.33</td>
</tr>
</tbody>
</table>

TABLE 1 : Changing of resistances.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Resistance (k\Omega) (S10F)</th>
<th>Resistance (k\Omega) (V10F)</th>
<th>Resistance (k\Omega) (V10S10F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.98</td>
<td>5.54</td>
<td>116.0</td>
</tr>
<tr>
<td>5</td>
<td>8.92</td>
<td>5.49</td>
<td>115.8</td>
</tr>
<tr>
<td>10</td>
<td>8.88</td>
<td>5.46</td>
<td>115.3</td>
</tr>
<tr>
<td>15</td>
<td>8.86</td>
<td>5.45</td>
<td>115.0</td>
</tr>
<tr>
<td>20</td>
<td>8.85</td>
<td>5.45</td>
<td>114.8</td>
</tr>
<tr>
<td>25</td>
<td>8.84</td>
<td>5.45</td>
<td>114.5</td>
</tr>
<tr>
<td>30</td>
<td>8.83</td>
<td>5.42</td>
<td>114.45</td>
</tr>
</tbody>
</table>
Figure 2 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$_2$O$_5$ and composite system respectively. Figure 3 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$_2$O$_5$ is showing sensitivity S= 2.16 at room temperature, but recovery of the both pure are 8 minute and 3 minutes respectively which could be observed in figures. Figure 2 also 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:  
\[ S = \frac{(R_a-R_g)}{R_a} \]
Where: S - Sensitivity, R$_a$ - resistance of sample in dry air i.e. initial resistance.  
R$_g$ - resistance of sample in SO$_2$ gas i.e. final resistance.

CONCLUSION

1. I-V characteristics of composite V$_2$O$_5$: SnO$_2$ which shows non linear behavior. This non linear behavior is may be due to formation of n-n junction in which SnO$_2$ act as n type and V$_2$O$_5$ act as n type semiconductor also. 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.

2. Room temperature gas sensing for time period of 30 seconds is studied for pure SnO$_2$, pure V$_2$O$_5$ 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.

3. 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$_2$O$_5$. So it always try to comes in stable state so might be showing fast recovery.

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

REFERENCES


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Full Paper