Synthesis, characterization and CO$_2$ gas sensing response of SnO$_2$/Al$_2$O$_3$ double layer sensor

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Tin dioxide (SnO$_2$) material changes its properties depending on the ambient gas which can be utilized as gas sensing materials. Usually changes in electrical resistance/conductance in response to environmental gases are monitored. SnO$_2$ and double layer (SnO$_2$/Al$_2$O$_3$) sensors have been prepared by screen-printing technique on glass substrate. The sensors were used for different concentration (ppm) of CO$_2$ gas investigation at different temperature. The sensing response (sensitivity) of SnO$_2$/Al$_2$O$_3$ double layer sensor was found to be higher, compared with pure SnO$_2$ sensor. The average grain size of SnO$_2$ was determined from XRD pattern and found to be 120.7 nm. The activation energy ($E_a$) of first order reaction ($n=1$) for SnO$_2$ has been found to be 72.06 kJ/g-mol from endo DDTA and 325.95 kJ/g-mol from exo DDTA. The microstructure of SnO$_2$ has been studied from SEM analysis. The oxygen ions adsorb onto the surface of material removes electrons from the bulk and create a potential barrier that limits electron movement and resistivity. When exposed to an oxidizing gas such as CO$_2$ then it is chemisorbed on bridging oxygen atoms with the formation of a surface carbonate, subsequently increasing the barrier height and resistivity.

Keywords: SnO$_2$, Al$_2$O$_3$, Screen-printing technique, CO$_2$ gas, Double layer sensor, Microstructure

1 Introduction

Chemical gas sensors have been of much scientific and commercial interest already for several decades. New application areas provoke a steady development of new sensor types to meet the additional requirements. At the same time, new sensor types open up new application areas. In spite of the large number of already available sensing layers for chemical gas sensors and the existing technology, new materials need to be tested for special applications and new sensors are being developed.

In recent years, a great attention has been paid to the development and application of environmental gas sensors. CO$_2$ is very difficult to detect by conventional gas sensor due to high stability at ambient temperature. Many efforts have been made to develop chemical sensors based on solid-state technology, exploiting either the surface characteristic or the bulk conduction properties of ceramics. Based on the surface characteristic, there are two kinds of sensors, capacitive and resistive type (chemoresister).

Maier et al.$^1$ had first time demonstrated the CO$_2$ gas detection, since then many researchers.$^2,6$ have reported CO$_2$ gas detection by using metal oxides (MOXs), zeolites and conducting polymers (CPs). Since the chemical property of CO$_2$ is stable, it was thought that the MOX semiconductor-type sensor could not be used for determining CO$_2$, while the research.$^7$ reported SnO$_2$, when alkaline oxide is added becomes sensitive to CO$_2$ to some degree, but its preference to CO$_2$ is bad and the stability is not ideal. Ishigara et al.$^8$ have found that the complex oxide compound of BaTiO$_3$ and PbO is sensitive to CO$_2$ and developed a semiconductor capacitive-type sensor for CO$_2$ gas. Since then, more sensors for CO$_2$ gas have been introduced. SnO$_2$ has various specific and unique properties, which make this material very useful in many applications.$^6$ Polycrystalline thin and thick films of SnO$_2$ have been extensively used for production of resistors.

In the present work, SnO$_2$ and double layer (SnO$_2$/Al$_2$O$_3$) sensors have been prepared by screen-printing technique on glass substrate. The sensors were used for different concentration (ppm) of CO$_2$ gas investigation at different temperature. The characterisation of SnO$_2$ was done through XRD, SEM and TG-DTA to know about the material structure and thermal stability, which may be related to its detection properties.

2 Experimental Details

In the preparation of gas sensors, AR grade metal oxide powders (SnO$_2$ and Al$_2$O$_3$) were used. The powders were calcined at 800°C in automatically
temperature controlled muffle furnace (Gallenkamp, British made) for 4 to 5 h. The powder of these materials was mixed in pestle and mortar before and after calcinations so that fine homogeneous powder will be formed. XRD pattern of SnO$_2$ was recorded on a Philips-1730 (PANalytical) X-ray diffractometer using CuK$\alpha$ source ($\lambda = 1.54\text{Å}$). The diffractogram was in the term of 2$\theta$ at continuous scan type at step size $2\theta = 0.0170^\circ$.

TG-DTA was carried out on a Perkin Elmer-7 thermal analyzer (TG/DTA) under an inert atmosphere. The reference was an empty aluminium pan and a flow of argon was set at 200 ml min$^{-1}$. A small amount of material (3-9 mg) was placed in a sample aluminium pan. The temperature scan started from room temperature to 900°C and a heating rate was set at 10°C min$^{-1}$. The morphology of SnO$_2$ has been investigated by using JEOL-JSM (model-5200) SEM instrument. An acceleration voltage of 15 kV was used in the SEM measurement. The micrograph was recorded with a resolution of 1 $\mu$m and 10000 X magnifications.

The screen consists of finely woven polyester mesh having 160 openings per linear inch, mounted under tension of a wooden frame. The binder was prepared by thoroughly mixed 8-wt% butyl carbitol with 92-wt% ethyl cellulose. The paste (ink) for screen-printing was prepared by thoroughly mixing 60 wt% powder of material with 40 wt% binder in agate and mortar so that a thick and coherent paste is produced. The paste thus prepared was screen-printed onto a chemically cleaned glass substrate of size 75 mm $\times$ 25 mm, the films then allowed to stand in air for 24 h so that the ink can level off and settle. The dried films were heated at 120-150°C for 2-3 h. During this stage, the volatile organic solvent was removed via decomposition and the prints adhered to the substrate. Therefore, the ink solvent does not diffuse in samples.

For Al$_2$O$_3$ based films, paste of Al$_2$O$_3$ was screen printed onto a chemically cleaned glass substrate and dried at room temperature for 24 h and then heated at 120-150°C. The sensing layer of material then screen-printed onto already printed Al$_2$O$_3$ film and following the steps of adequate heat treatment. For measuring the resistance, electrical contacts of silver paint were deposited on adjacent sides of SnO$_2$ layer. The voltage divider method was used to measure electrical resistance of sensor films in test gas.

The gas chamber having dimensions 30 cm $\times$ 30 cm $\times$ 30 cm with attached CO$_2$ gas flow meter (Flowtron make, India having range 1 to 10 ml min$^{-1}$) was used for keeping the sensors for testing. The gas flow was adjusted to 2 ml min$^{-1}$ so that a gas concentration (ppm) with time has been obtained. At one side of chamber, a small airtight hole was made for keeping the samples. The sample holder with attached iron heater and thermocouple was fitted at centre of the chamber. For constant pressure of gas, gas regulator was attached to the gas inlet. The readings were carried out in a CO$_2$ gas environment at different ppm level and various temperatures.

### 3 Results and Discussion

Figure 1 shows the characteristic XRD pattern of SnO$_2$ calcined at 800°C for 4-5h. The $(h k l)$ values are obtained by using 2$\theta$ and $d$-values from XRD pattern. The main peaks in the diffractogram are indexed as (110), (101), (200), (211), (220), (310), (301) and (321) corresponding to Bragg’s angles $2\theta$ = 26.61, 33.90, 37.98, 51.94, 54.78, 62.05, 66.18 and 78.96°. These are the prominent peaks of SnO$_2$ and correspond to the cassiterite phase (JCPDS No. 22150). The average grain size, determined from XRD pattern using Scherrer formula [10] of SnO$_2$, is about 120.7 nm.

Figure 2(a and b) shows the TG-DTA plots and simultaneously recorded derivative of DTA (DDTA) curves of SnO$_2$ material. A significant loss of weight is observed from room temperature (RT) to 550°C without plateau with a loss of about 5.2%. The total rate of decomposition is found to be 0.466$\times$10$^{-3}$ mg/°C and total loss is 5.74%. The DTA data shows an endothermic peak at 38°C associated with surface water loss and a small exothermic peak at 495°C is observed which may be attributed to phase change.

If the DTA curve and its derivative (DDTA) are simultaneously recorded, the two inflection points i.e. the maximum and the minimum slopes of the DTA

![Fig. 1 — XRD pattern of SnO$_2$ calcined at 800°C for 4-5h](image-url)
peak correspond to the maximum and minimum of the DDTA double peak, are obtained\textsuperscript{11}. Therefore, the temperature $T_{f1}$ and $T_{f2}$ can be easily and exactly detected on the DDTA curve.

The temperatures of double peak, $T_{f1} = 61^\circ C$ and $T_{f2} = 38^\circ C$, on DDTA curve [Fig. 2(b)] for endothermic peak of DTA curve (Fig. 2a) are observed. Similarly, for exothermic peak, $T_{f1} = 495^\circ C$ and $T_{f2} = 525^\circ C$ are observed for SnO$_2$.

The activation energy ($E_a$) of first order reaction ($n = 1$) using temperatures of two inflection\textsuperscript{12-14} points $T_{f1}$ and $T_{f2}$ was derived from Eq. (1) and found to be 72.06 kJ/g-mol from endo DDTA and 325.95 kJ/g-mol from exo DDTA.

$$\frac{E_a}{R} \left( \frac{1}{T_{f1}} - \frac{1}{T_{f2}} \right) = 1.92$$

... (1)

where $R$ is the gas constant (8.31 J/g-mol K).

Figure 3 shows the randomly distributed SnO$_2$ grains, calcined at 800 °C for 4-5 h with larger size and shape distribution. The large number of grains which leading to high porosity and large effective surface area available for adsorption of gas species. The image clearly shows the spherical morphology with certain degree of elongation and the sensing material is found to be highly porous. Macro-pores of material are therefore, considered as a good candidate for sensing application. The pore size (PS) varies from ~50 nm to 1 µm. The average grain size seen from micrograph varies from ~100 to 500 nm.

The sensor response (sensitivity) is defined as in Ref (15). The SnO$_2$ sensor also shows maximum resistance change at RT (Fig. 4a) but its sensitivity is found to be higher at 333 K (Fig. 4b), which is the operating temperature of sensor. The maximum value of average sensor resistance change per ppm of CO$_2$ is found to be 3.5×10$^6$ Ω/ppm at 303 K.

The SnO$_2$/Al$_2$O$_3$ sensor shows a continuous variation in sensitivity without saturation. The
Thus, the Al$_2$O$_3$ sensor surface, resulting in a change in concentration of adsorbed oxygen. At lower temperature (< 150°C), the average sensor resistance change per ppm of CO$_2$ in the range 303-343 K (Fig. 5b) and maximum value of sensor decreases with increasing temperature in the range 303-343 K. The sensitivity of pure SnO$_2$ material is enhanced in Al$_2$O$_3$ based sensor to CO$_2$ gas. The average grain size of SnO$_2$ was determined from XRD pattern and found to be 120.7 nm. The activation energy ($E_a$) of first order reaction ($n=1$) for SnO$_2$ was found to be 72.06 kJ/mol from endo DDTA and 325.95 kJ/mol from exo DDTA. SEM study reveals that the large number of grains leading to high porosity and large effective surface area are available for adsorption of gas species. The micrograph shows the spherical morphology with certain degree of elongation and the sensing material is highly porous. The pore size (PS) varies from ~50 nm to 1 μm. From mechanism, it is concluded that the CO$_2$ is chemisorbed on bridging oxygen atoms with the formation of a surface carbonate thus increasing the barrier height and resistivity.

4 Conclusions

SnO$_2$ and double layer (SnO$_2$/Al$_2$O$_3$) sensors were prepared by screen-printing technique on glass substrate. The sensors were used for different concentration (ppm) of CO$_2$ gas investigation at different temperature. The SnO$_2$ sensor showed a maximum resistance change at RT but its sensitivity is found to be higher at 333 K, which is the operating temperature of sensor. The SnO$_2$/Al$_2$O$_3$ sensor shows a continuous variation in sensitivity without saturation. The sensitivity of double layer sensor decreases with increasing temperature in the range 303-343 K. The sensitivity of pure SnO$_2$ material is enhanced in Al$_2$O$_3$ based sensor to CO$_2$ gas. The average grain size of SnO$_2$ was determined from XRD pattern and found to be 120.7 nm. The activation energy ($E_a$) of first order reaction ($n=1$) for SnO$_2$ was found to be 73.06 kJ/mol from endo DDTA and 325.95 kJ/mol from exo DDTA. SEM study reveals that the large number of grains leading to high porosity and large effective surface area are available for adsorption of gas species. The micrograph shows the spherical morphology with certain degree of elongation and the sensing material is highly porous. The pore size (PS) varies from ~50 nm to 1 μm. From mechanism, it is concluded that the CO$_2$ is chemisorbed on bridging oxygen atoms with the formation of a surface carbonate thus increasing the barrier height and resistivity.

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