Journal of Electron Devices, Vol. 21, 2015, pp. 1849-1853

© JED [ISSN: 1682 -3427]

Journal of Electron Devices
www.jeldev.org

TIN OXIDE AND TITANIUM DIOXIDE BASED CO_2 GAS SENSOR

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Received 19-02-2015, online 30-05-2015

ABSTRACT

The influence of CO_2 gas concentration on the transport properties of SnO_2-10Al_2O_3-10TiO_2 oxide thick films has been studied. From the X-RD spectra the average crystallite size of the samples is found to be of the order of 10.80 nm to 56.05 nm and shows polycrystalline and granular nature. For a fixed concentration of gas the sensitivity decreases with increase in temperature, but increases with increasing concentration of CO_2 gas. Transient response of the samples was studied. The resistance of all the samples increases by increasing the concentration of CO_2 gas, due to oxidization process on the surface of the material.
Keywords: Metal oxide thin films, electrical conductivity, transient response, CO_2 gas Sensor.

I. INTRODUCTION

The hetero-structure mechanism and the amorphous nature of the samples are important for the sensing devices. Ceramic and amorphous materials may be the best sensors for sensing the present gases. Most of the research workers have studied the electrical resistance of the material in presence of CO_2 gas environment. Today multi–functioning sensors are available in the market but now there is a need to develop the best sensor for sensing the single gas only. The semiconductor metal oxide materials are generally used in the form of wafer (thin pellet) or film (thin or thick) deposited on a substrate (glass, silica, silicon, alumina, steatite etc.). Gas sensors in the form of thin or thick films seems to be more promising detectors over the pellet form, because they are potentially of low cost, rugged and have low consumption of electric power and more active surface area.

A sensor array comprising of three chemical gas sensors was evaluated to predict the concentrations of O_2, CO and CO_2 in a gas stream at 600^{o}C [1]. The sensors in the array included a resistance-based 2% CuO/10% La_2O_3/TiO_2 material and yttrium stabilized zirconium (YSZ) sensor with a metal/metal oxide internal reference electrode and a lithium phosphate-based sensor. Electrochemical impedance spectroscopy (EIS) was used to study the electrical properties of heat treated electrochemical gas sensors [2]. In the present paper solid solution of metal oxides SnO_2-10TiO_2-10Al_2O_3 in the form of thick films is selected. The pure TiO_2 and Al_2O_3 are mixed with SnO_2 for the improvement of temperature characteristic and stability respectively.

II. EXPERIMENTAL DETAILS

The thick films of tin oxide (SnO_2), titanium oxide (TiO_2) and alumina (Al_2O_3) were prepared by screen-printing technique on chemically clean optically plane glass substrate. The X-ray diffraction (XRD, Rigaku X-ray diffractometer, Japan) analyses of thick films was conducted using Cu Kα radiation to determine the different phases and the grain size. The crystallite size was calculated from the full width at half maximum of the first peak using the Scherrer's formula [3].

The thickness of the sensor films was measured by Digimatic Outside Micrometer (Series-293, Japan) having a resolution of ±0.001mm and found to be 7.45, 40.09 and 73.34 μm for (SnO_2-10TiO_2-10Al_2O_3) solid solution, pure SnO_2 and pure TiO_2 sensors respectively. The resistance of the sensor was measured by voltage drop method adopted by Yawale *et al* [4, 5]. By knowing sensor resistance the sensitivity was calculated.

III. RESULTS AND DISCUSSION:

Tin oxide (SnO_2) is a wide energy gap n-type semiconductor. It is used as sensor because of its chemical and mechanical stability. The fig.1 shows the XRD spectra of (SnO_2-10TiO_2-10Al_2O_3) solid solution and shows polycrystalline and granular nature of the selected oxides. From fig. 1 it is observed that XRD spectra contains 10–15 peaks which are due to SnO_2 and TiO_2. The (*h*, *k*, *l*) values are obtained by using 2θ and d-values. Tin dioxide has one stable state called as rutile. Anatase phase of TiO_2 changes to rutile when heated above temperature 500 ^{o}C along with SnO_2 and Al_2O_3 [6, 7]. So the structure of TiO_2 and SnO_2 is same. The lattice parameter values obtained for SnO_2 and TiO_2 are $a = b = 4.7382$ ^{o}A and $c = 3.1871$ °A with c/a ratio of 0.6726 and $a = 4.5933$ °A and $c = 2.9595$ °A with c/a ratio of 0.6442, respectively. These values are in agreement with the values reported in references [8, 9]. The rutile phase is stable and because of the same structure of SnO_2 and TiO_2, the space group and atom location sites changes the Ti^{4+} by Sn^{4+} metallic cation. Similarly the Al_2O_3 which is added as stabilizer to SnO_2–TiO_2 material, forms hexagonal phase with $a = 4.758$ °A and $c = 12.925$ A°. These phases are playing very important role for sensing the CO_2 gas [10, 11].

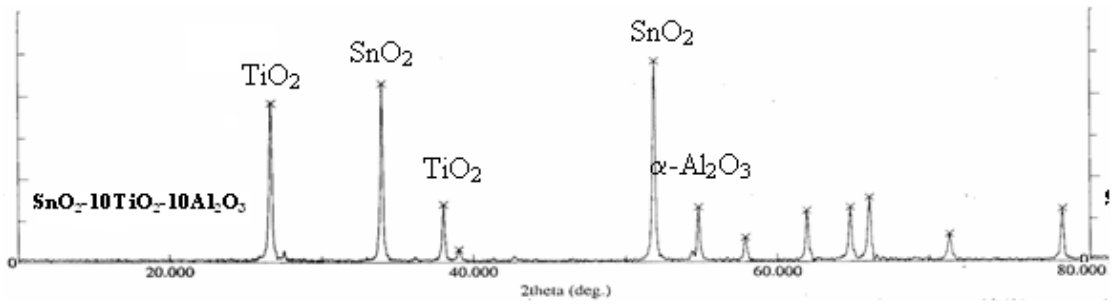

Figure 1: X-RD spectra of (SnO_2-10TiO_2-10Al_2O_3) thick film

The average crystallite size calculated using FWHM and ON time and OFF time of various sensor parameters are reported in the table 1.

Table 1: Crystallite size and response time of sensors.

SN	Composition (mol %)	crystallite size (nm)	Sensitivity (s) at 500ppm at 313K	Response Time (sec)	
				ON time	OFF time
1	Pure SnO_2	56.05	10.19	90	105
2	Pure TiO_2	10.80	5.57	75	105
3	SnO_2-10TiO_2-10Al_2O_3	10.80	26.07	60	105

Fig. 2 shows the variation of sensitivity with change in concentration of CO_2 gas at different temperatures 313K, 323K, 333K and 343K for sensor (SnO_2-10TiO_2-10Al_2O_3). From figure 2, it appears that the sensitivity decreases by increasing temperature of thick films. At lower concentration of gas a linear behavior is observed whereas at higher concentration, the plot deviates from linearity. At higher temperature range the change in the sensitivity with concentration is small. The sensor sensitivity (S) is proportional to the number of active centers on the surface of sensor. The number of active centers is the product of surface area and surface density of the active centers. The specific surface is a ratio of surface area to mass of the sensor therefore; the sensor sensitivity is proportional to the product of specific surface, density of active centers and the sensor mass. So if the specific surface is more, the number of active centers will be more and therefore the higher sensitivity of the material [12]. The TiO_2 doped polycrystalline SnO_2 sensor shows higher sensitivity just as in metal oxide (SnO_2-10TiO_2-10Al_2O_3) thick film.

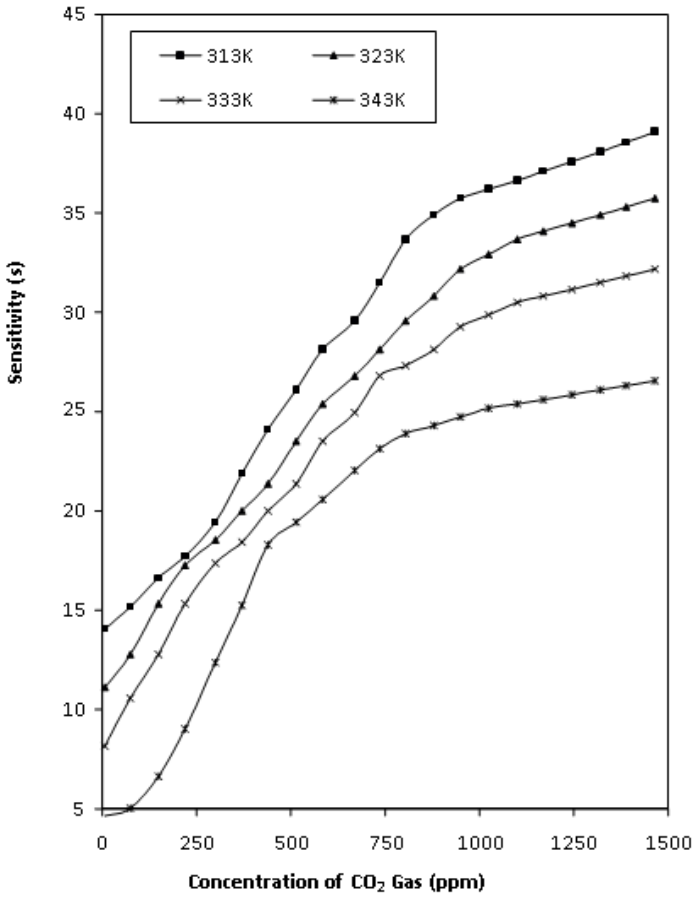

Figure 2: Variation of sensitivity with concentration of CO_2 gas at different temperatures for SnO_2-10TiO_2-10Al_2O_3 thick film.

Fig. 3 shows the variation of sensitivity with temperature at constant concentration of CO_2 gas (1465ppm) for the thick film (SnO_2-10TiO_2-10Al_2O_3), pure SnO_2 and pure TiO_2. These plots are found to be linear. It is seen that the sensitivity of solid solution is more than the pure SnO_2 and pure TiO_2 at higher and lower concentration of CO_2 gas.

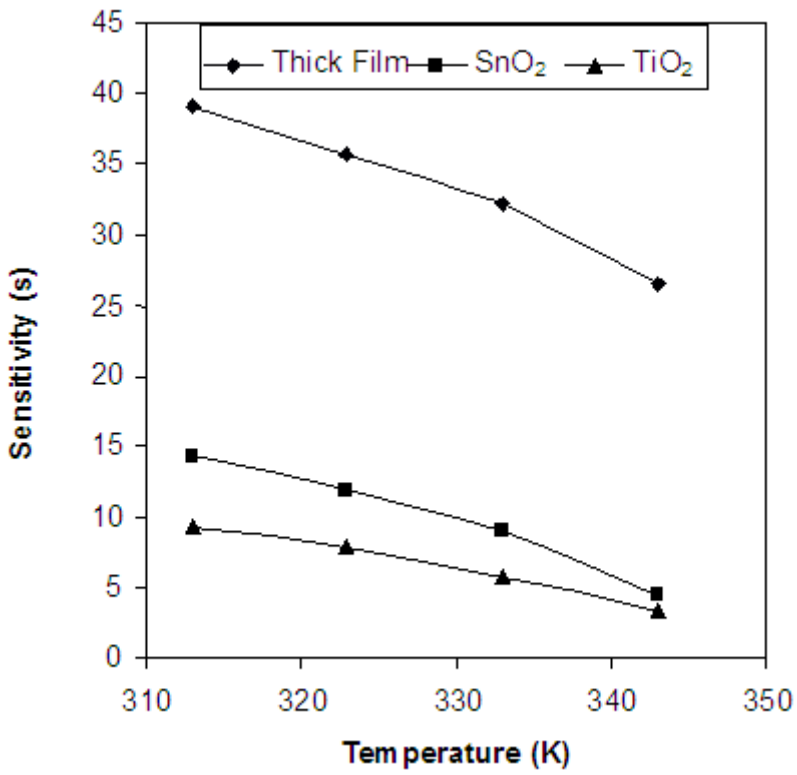

Figure 3: Variation of sensitivity with temperature at constant concentration of CO_2 gas (1465ppm)

Fig.4: shows the variation of sensitivity with change in concentration of CO_2 gas for the solid solution, SnO_2 and TiO_2 thick films at constant temperature (313K). In all the films the sensitivity increases linearly for the lower concentration range but for higher concentration range it deviates from linearity. It is also observed that the sensitivity change in solid solution thick film is more than SnO_2 and TiO_2 films.

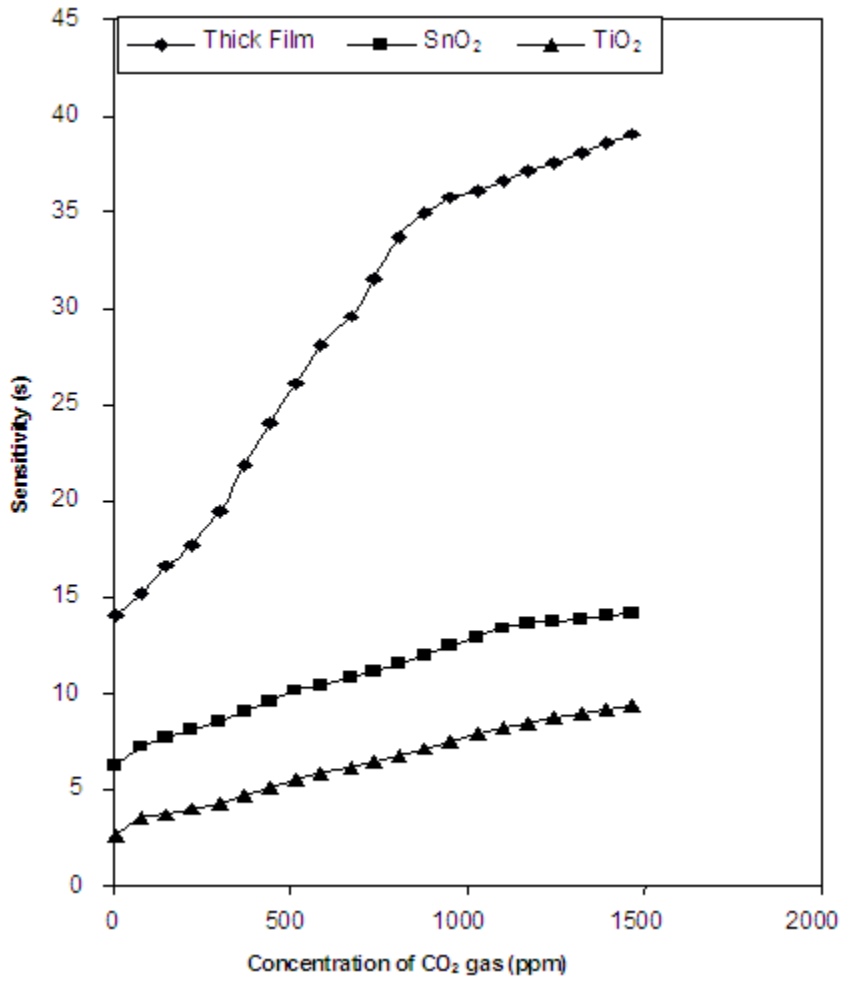

Figure 4: Variation of sensitivity with concentration of CO_2 gas at constant temperature (313K)

Fig. 5 shows the transient response of the solid solution thick film, SnO_2 and TiO_2 at 500-ppm concentration of CO_2 gas. It is observed that the solid solution has 75 s ON time and 105 s OFF time whereas for the pure SnO_2 film the ON time and OFF time is 90 and 105 s respectively. But it is also noted that, pure TiO_2 has minimum OFF time and higher ON time. This shows that the addition of TiO_2 in SnO_2 reduces the ON time of the sensors.

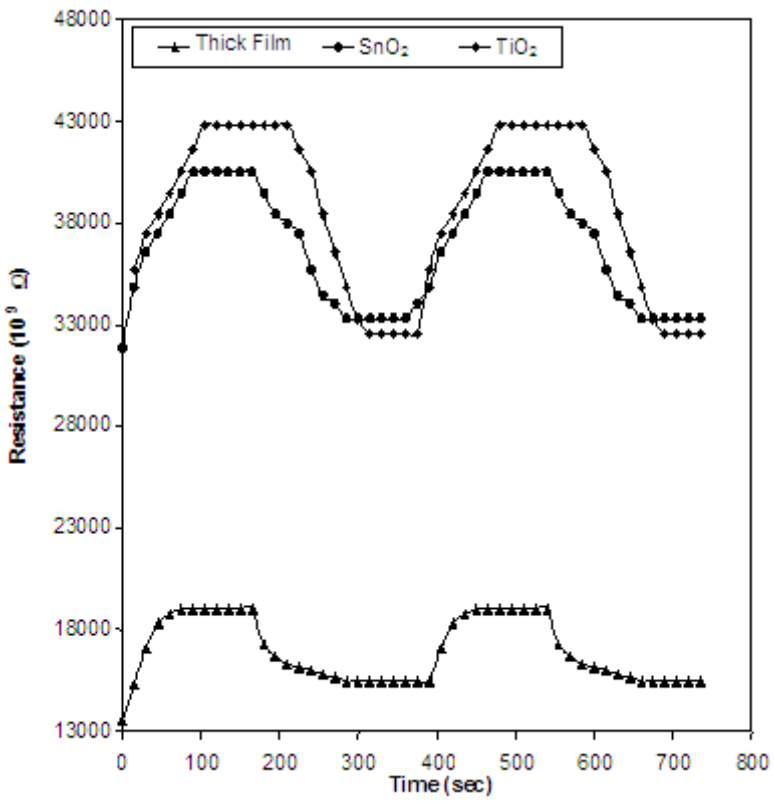

Figure 5: The transient response of CO_2 gas at constant concentration (500ppm)

At temperature 313 K, the change in resistance in presence of CO_2 gas is found to be small, whereas at 343 K the resistance change is appreciable. Addition of Al_2O_3 and TiO_2 in pure SnO_2 never affect the nature of the curves, only the resistance change is observed. The sensitivity of the (SnO_2-10TiO_2-10Al_2O_3) thick film increases by increasing the concentration of CO_2 gas. The surface conductance effects are dominant in sensing the gases. The electrical conductivity (σ) depends on the electron concentration 'n' and this concentration is related to the equilibrium constant and the partial pressure of the gases. The CO_2 gas has oxidizing properties and it leads to an oxidization of material therefore, the conductivity of the material reduces [12-14]. The possible mechanism for CO_2 gas detection in SnO_2 material is based on reactions that occur at the sensor surface, resulting in a change in concentration of adsorbed oxygen. At lower temperature (<150^oC), oxygen adsorption at the surface is mainly in the form of O^{2-}. 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 [15], subsequently increasing the barrier height and the resistivity. Under the presence of O_2 atmosphere, the sensing material chemisorbs gas on its surface. Oxygen can be adsorbed in the several forms such as O^-_2, O^-, O^{2-} while, CO absorbs O atom from the surface becoming CO_2.

The small amount of Ti can be disperse at grain boundaries, directly or indirectly affected the density of centers which are active for gas adsorption. The grain size effect i.e. average crystalline size is also important for the sensing mechanism. It has been reported [16-19], that the sensitivity decreases with crystallite size in case of hydrogen and carbon monoxide. The granular and polycrystalline structure plays very important role in the electrical properties. The films, which have a grain size of nanometer order, they facilitated the adsorption process of gas like water molecule in the humidity sensors [7]. In this way the adsorption of CO_2 gas on the surface of thin film takes place through chemisorptions process.

IV. CONCLUSION

The solid solution has been polycrystalline nature and crystallite size found to be order of 10.80 nm. The sensitivity of solid solution is higher than the pure SnO_2 and pure TiO_2. This shows that by the addition of TiO_2 and Al_2O_3 temperature characteristic and stability of the sensor improved. The ON time for this sensor is 60s and OFF time is 105s at 500ppm of CO_2 gas. The resistance of the film increases in presence of CO_2 gas due to decrease in the electron concentration at the surface of the sensor because of oxidization of the material.

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