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Surface Modified TTO Thick Film Resistors for NH_3 Gas Sensing

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Abstract: $Ti_{0.8}Sn_{0.2}O_2$-Titanium tin oxide (TTO) compound was prepared by using mechanochemical processing. AR grade $TiCl_3.2H_2O$ (0.8 M) and $SnCl_4.5H_2O$ (0.2 M) were mixed followed by calcination and ball milling. As prepared TTO was then used as starting material to fabricate the sensors in thick film form. Thick films were prepared by screen-printing technology on glass substrate. The dipping technique was used to obtain surface-cupricated TTO films in which copper was incorporated as additive. The thick films so obtained were fired at 550°C. The characterization of the films was done by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The gas response measurements were carried out as function of operating temperature (200-400°C) for different gases. These films were found to be most sensitive to NH_3 gas. Surface cupricated film showed high gas response, fast response and quick recovery to NH_3 gas. The result indicated that Cu modification would be responsible for improving stability and gas response of the sensor. The film dipped for 10 minute was observed to be most sensitive to NH_3 gas at an operating temperature 300°C.

Keywords: $Ti_{0.8}Sn_{0.2}O_2$ (TTO); Thick films; Cuprication; NH_3 gas sensor; Gas response; Selectivity.

1. Introduction

Toxic and harmful gases cause atmospheric pollution. The sensors are required basically for monitoring of trace gases in environment. In order to detect measure and control these gases; one

should know the amount and type of gases present in the environment. Thus the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies.

Among the most toxic and hazardous gases, it is necessary to detect and monitor the ammonia gas because this is enhance in the agricultural sector by the addition of large amounts of NH_3 to cultivated farmland in the form of fertilizers. However when too much NH_3 is added to the soil, this leads to acidification, eutrophication change in vegetation [1] and increase in NH_3 concentration [2]. Most of NH_3 is converted to ammonium ions because most soils are slightly acidic [3]. In order to control such emissions, the study of chemical sensors with suitable sensing performances has focused increasing interest [4].

Semiconductor gas sensors have been widely investigated for gas sensing application due to their low cost, good performances and easy implementation. It is known that titanium dioxide TiO_2 and SnO_2 are an important semiconductors utilize explosively in many industries. Some of the well-known materials for NH_3 sensors are pure ZnO [5,6,7], SnO_2 [8], TiO_2 [9], Cr_2O_3 doped TiO_2 [10]. It has reported that TiO_2 shows response to the hazardous gases such as carbon monoxide (CO) [11-13], NO_2 [14-16] and organic materials like Benzene [17] etc.

This article deals with preparation procedure of thick films of unmodified and surface modified $Ti_{0.8}Sn_{0.2}O_2$ (TTO) by screen printing technique and their gas sensing performance.

2. Experimental

2.1. Preparation of TTO powder

Titanium tin oxide compound was prepared by using mechanochemical processing. AR grade $TiCl_3.2H_2O$ (0.8 M) and $SnCl_4.5H_2O$ (0.2 M) were mixed thoroughly. The mixture was slowly calcined at 1000^oC for 10 hrs. The product was then ball milled to obtain homogeneous solid solution of TTO and to ensure sufficiently fine particle size.

2.2. Preparation of TTO thick films

The thixotropic paste was formulated by mixing the fine powder of TTO with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents, such as butyl cellulose, butyl carbitol acetate and turpineol etc. The ratio of inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen printed [18,19]. The films were fired at 550^oC for 30 min. Silver contacts are made for electrical measurements.

2.3. Preparation of cupricated TTO thick films

The cupricated TTO thick films were obtained by dipping the pure TTO thick films in 0.01 M aqueous solution of cupric chloride for different intervals of dipping time such as 5, 10, 20 and 30 min. These films were dried under IR-lamp. These films are fired at 550^oC for 30 min.

The films so prepared are termed as “surface cupricated” films. Thus sensor element with various wt % of CuO was prepared. Cupricated films so obtained were examined for gas sensing performance.

2.4. Characterization of gas sensors

The crystalline structure was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK_α radiation with a wavelength 1.5418 Å. Microstructure of pure and surface modified films was examined by scanning electron microscopy (Leica Stereoscan 330 model) and the amount of copper oxide incorporated on the surface of the films was determined by energy dispersive X-ray analysis (Table 1). Electrical and gas sensing characteristics were measured using a static gas sensing system.

2.5. Measurement of gas response, selectivity, response and recovery time

Gas response is defined as the ratio of change in conductance of the sample on exposure to gas to the conductance in the presence of air.

$$S = \frac{G_g - G_a}{G_a}$$

where G_a is the conductance of sensor in air and G_g is the conductance of sensor in presence of gas.

The ability of the sensor to respond to a specific gas in the presence of other gases is the selectivity.

The time taken by the sensor to attain the 90 % of change in conductance on exposure to a gas is response time while the time taken by the sensor to get back to 90 % of the original conductance in air is the recovery time.

3. Results

3.1. XRD of TTO thick films

Figure 1 shows the X-ray diffractogram of TTO thick film. The average grain size was determined by using Scherrer formula and was estimated to be 61 nm.

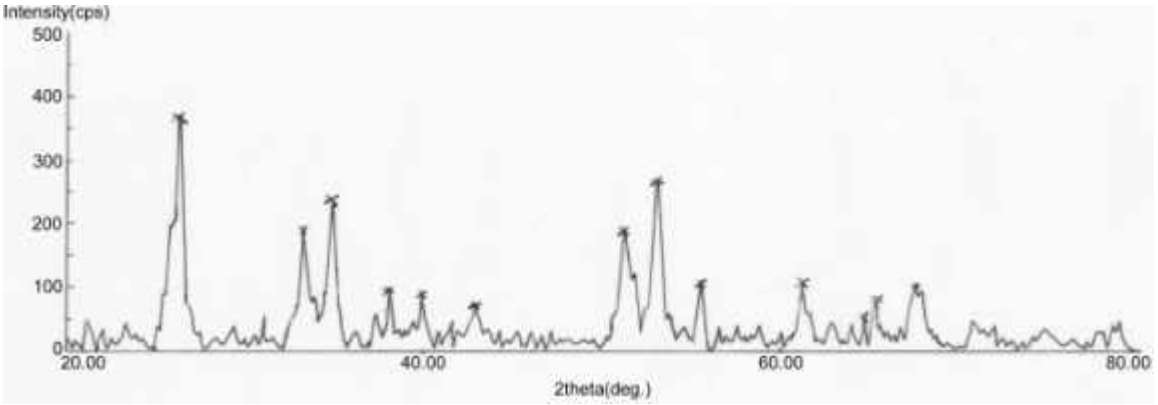

Fig. 1. XRD of TTO thick films slowly calcined at 1000°C for 10 hrs.

3.2. Surface morphology of unmodified and modified TTO thick films

Fig.2(a), 2(b) and 2(c) depict the micrograph of unmodified, most sensitive modified (10 min) film and a film modified for the largest interval of time (30 min) of TTO respectively. Unmodified film (fig. 2(a)) consists of randomly distributed grains with larger size and shape distribution. Fig. 2(b) depicts the microstructure of modified film (dipping time 10 min) consisting of uniformly distributed smaller size and shape. Figure 2(c) indicates larger grains as compared to the grains associated with fig. 2(b).

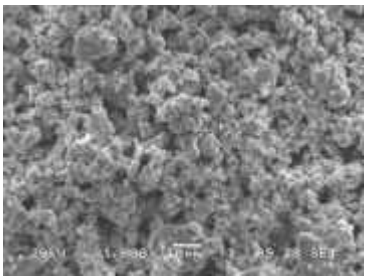

Fig. 2(a). A micrograph of unmodified TTO thick films.

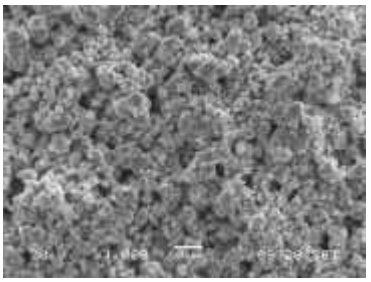

Fig. 2(b). A micrograph of modified (10 min) film.

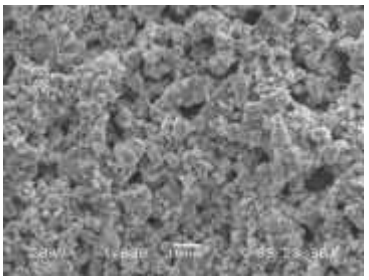

Fig. 2(c). A micrograph of modified (30 min) film.

3.3. Gas-sensing characteristics

3.3.1. Optimization of dipping time

Fig. 3 shows the variation of response of modified film to 1000 ppm of NH_3 with dipping time. The response increased with increasing the time of dipping to attains the maximum (S=90) at 10 min, and then decreased with a further increase of dipping time. The amount of CuO at dipping time 10 min would be optimum to cover the film surface and to make a sufficient number of Cu sites available for adsorption of oxygen species. Larger the number of oxygen ions adsorbed on the film surface, faster would be the oxidation of NH_3 gas exposed on the surface.

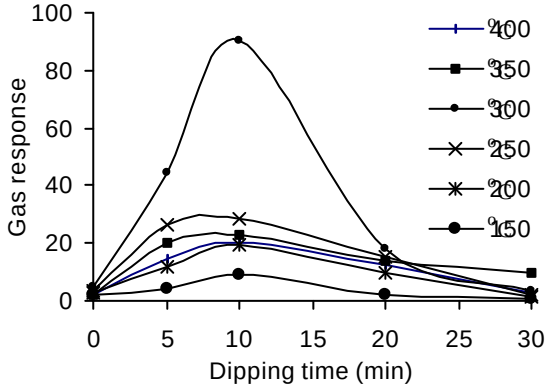

Fig. 3. Variation in response to 1000 ppm of NH_3 of TTO thick films with surface modification, fired at 550°C, at different operating temperatures.

3.3.2. Optimization of operating temperature

Figure 4 shows the variations of response to 1000 ppm NH_3 of the to unmodified and modified TTO thick films fired at 550°C with operating temperatures. The response increased with increasing the operating temperature to attains the maximum at 300°C, and then decreased with a further increase of operating temperature. The modified sensor (10 min) showed highest response (S=90) at 300°C.

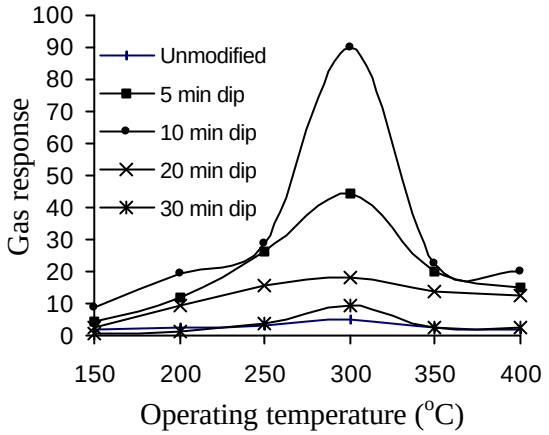

Fig. 4. Gas response to 1000 ppm of NH_3 to unmodified and modified TTO thick films fired at 550°C with operating temperatures.

3.3.3. Responses to various gases of TTO thick films

Fig. 5 shows the variation of gas response of the TTO films (fired at 550°C) to various gases with operating temperatures ranging from 150 to 400°C. For ammonia, gas response goes on increasing with operating temperature, attains its maximum at 300°C and then decreases with further increase in operating temperature. It is clear from figure that, the sensor gives maximum response to H_2 (15.11) at 250°C; to NH_3 (90) at 300°C; to Ethanol (19.33) at 300°C; to LPG (1.37) at 350°C; to CO_2 (13.68) at 350°C; and to Cl_2 (9.2) at 350°C.

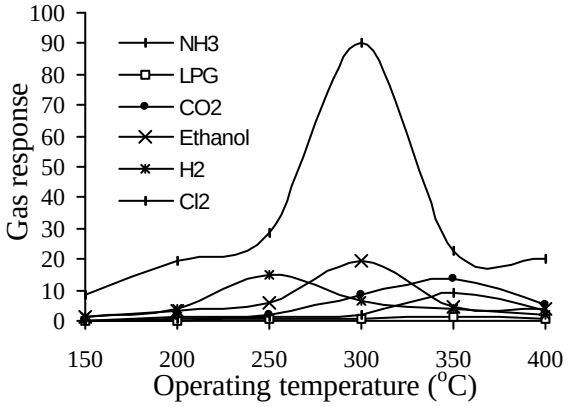

Fig. 5. The response of sensor to various gases with operating temperature.

3.4. Selectivity of modified TTO thick films

The ability of modified TTO sensor to identify NH_3 gas in the presence of other gases was checked. The sensor was selective to NH_3 gas as shown in Fig. 6.

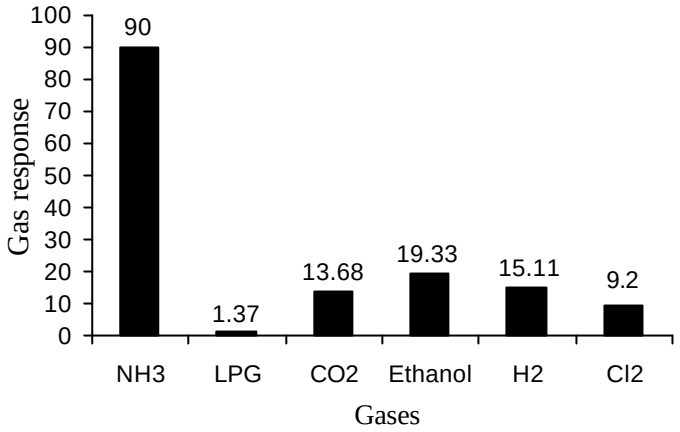

Fig. 6. Selectivity to NH_3 gas.

The modified TTO was observed to be highly selective to NH_3 against LPG, CO_2, Ethanol Cl_2 and H_2 gases. Due to cuprication of TTO the gas response to NH_3 was enhanced as compared to unmodified TTO.

4. Discussion

It is known that the atmospheric oxygen adsorbs on the surface of semiconductor in the form of O^- and O^{2-} thereby decreasing conduction. Atmospheric oxygen takes an electron from the conduction band of the TTO and adsorbs as O^-. The reaction is as follows:

$$O_2\{g\} + 2e^- \rightarrow 2O^-$$

In case of TTO, the carriers are believed to be due to excess TTO ions at the interstitial positions, due to oxygen vacancies, act as electron donors. Reducing gas like NH_3 reacts with adsorbed oxygen ions. The possible reaction is,

$$2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e^-$$

The point at which the sensitivity is maximum, is the actual thermal energy needed for the reaction to proceed. However, sensitivity decreases at higher operating temperature, as the adsorbed oxygen ions desorbed from the surface of the sensor [20]. Hence, there would be smaller number of oxygen ions present on the surface of TTO to react with the reducing gas and the sensitivity would fall at high operating temperature.

When the gas comes and adsorbs on the surface, there will be abstraction of electrons to the surface states caused by copper near the conduction band giving rise to Cu^{+2} oxidation states. The energy released during decomposition of the products is sufficient for electrons to jump into conduction bond of TTO causing on increase in the conductivity of the sensor. As the species desorbed from the surface, oxygen again adsorbs.

5. Conclusions

The conclusions are summarized as follows:

1. The NH_3 gas response, selectivity and response to various gases of unmodified TTO are poor.
2. The gas response of surface cupricated TTO to NH_3 was found to be larger than unmodified TTO sensor.
3. Higher NH_3 gas response of cupricated TTO could be attributed to surface copper misfits.
4. Surface modification is found to be highly suitable for selectivity control.

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