Spin coated tin oxide: a highly sensitive hydrocarbon sensor

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Abstract

The present investigation deals with the electrical response of ruthenium incorporated tin oxide thin film deposited by spin coating method, as a mean to improve the selectivity and sensitivity towards hydrocarbon gas. The thin film with ruthenium in tin oxide matrix exhibits remarkable sensitivity (s = 672) and selectivity towards hydrocarbon gas (Liquid petroleum gas) at the operating temperature of 300 °C. The X-ray diffraction (XRD) analysis of ruthenium incorporated tin oxide, fired at 400 °C reveals the polycrystalline nature, while pure tin oxide does not show crystalline nature at such a low firing temperature. A systematic evaluation of the surface coverage and morphology using techniques like energy dispersive X-ray analysis, scanning electron microscopy and XRD reveals a crucial role of the ruthenium species in the enhancement of sensitivity, selectivity and morphology. The correlation between ruthenium incorporation and the improvement in the sensitivity and selectivity towards hydrocarbon is discussed.

Key words: Tin oxide; Ruthenium; Spin coating; Hydrocarbon sensor

1. Introduction

In the last few years, sol–gel process has emerged as a promising technique for the synthesis of various thin film materials. The sol–gel process offers several advantages like low temperature processing, tailor making precursor, tunable porosity and thermal stability [1–3]. Incorporation of dopants is widely used for tailoring materials to achieve selective sensing [4–10], besides acting as catalyst they can modify the electrical transport properties of sensors by introducing the surface states, surface morphology and grain size.

Tin oxide has been reported for sensing toxic and inflammable gases including CO, H2, CO2, H2S, C2H5OH, and LPG [12–21]. It is widespread utility makes it essential to have a reliable and commercially viable hydrocarbon sensor. Tin oxide thin films can be prepared by techniques like evaporation, chemical vapor deposition, sputtering and spray pyrolysis, however, sol–gel technique appears to be simple and promising [11]. Various methods such as irradiation, incorporation of additives, controlling operating temperature, use of masks and filters [22,23] have been adopted to improve sensitivity. We have already discussed in our earlier communications the importance of surface modification in controlling the sensitivity and selectivity in tin oxide material [24,25]. Thin film in comparison to bulk faces limitation due to lower surface area, which plays a significant role in the gas sensing activity. This is one of the reasons for poor sensitivity of thin film material. However, thin film with high surface area has advantage like, fast recovery, lower energy input, device compatibility, miniaturization and overall cost effectiveness.

In the present publication we are reporting the use of simple spin coating technique for controlling the sensor performance by modifying the tin oxide matrix with ruthenium oxide. More specifically, tin oxide is anchored with ruthenium oxide to get the improved selectivity and sensitivity towards hydrocarbons (LPG). The main aim is to control the amount and
distribution of ruthenium oxide in the tin oxide matrix. The misfit regions have to be distributed at the grain boundaries in such a way so as to get a high sensitivity with good selectivity.

2. Experimental

2.1. Preparation of thin film of tin oxide by spin coating with ruthenium as an additive

Sols with long-term stability against gelation were obtained using tin tetrachloride as a precursor. Pure tin sols were prepared from tin tetrachloride (99.99%), distilled water, 1-propanol and 2-propanol (Aldrich 99.5%; water < 0.5%) in the volume ratio of 1:10:10:7. Firstly, 1-ml tin tetrachloride was added to 10 ml of 1-propanol, an exothermic reaction takes place. To this solution, after cooling, the other solution containing 3.0-ml water in 3.0 ml 2-propanol was added drop-wise followed by 1 h of continuous stirring. Finally, remaining 7.0 ml of water dissolved in 7 ml of 2-propanol was added followed by 1 h of continuous stirring. To this mother solution different composition of milli-molar concentration of ruthenium chloride was added under continuous stirring. The clear and homogeneous sols with different ruthenium concentration were thus obtained. These sols were then spin coated on the cleaned glass substrates at 1700 r.p.m. for 18 s followed by firing at an optimum temperature of 400\,^\circ\,C. The thickness of the film obtained after firing was in the range of 1100\,\AA\text{ (measured using Fizeau fringes method). The preparation parameters such as the amount of ruthenium and operating temperature were varied to establish the optimum composition of ruthenium in tin oxide to achieve the highest sensitivity.}

2.2. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was carried out on Philip 1730 machine using Cu K\(\alpha\) radiation for pure and ruthenated tin oxide films. Diffraction patterns were collected at a step of 0.02° (2\(\theta\)) using a fixed Cu K\(\alpha\) radiation. The background was subtracted with the linear interpolation method.

2.3. Scanning electron microscopy and energy dispersive X-ray analysis

The surface morphology and the semi-quantitative composition of different elements up to 1 \(\mu\)m depth were characterized by a Loea Stereoscan 440 model scanning electron microscopy (SEM) with a Keve model energy dispersive X-ray analysis (EDAX) system. The spin coated thin film samples were cut into 1 cm\(^2\) pieces and mounted on the sample holder after application of the electrically conducting paste. The samples were coated with a thin layer of gold in polaron coating unit E50000 to prevent charging of the samples. For comparative studies, the electron beam was kept constant while analyzing all the samples. The micrographs of the samples were recorded with a 20 kV electrical high tension and 25 pA current camera attached on the high-resolution recording unit.

2.4. Gas sensing experiments

The tin oxide films were cut into 1.0 \(\times\) 0.5 cm pieces. Silver contacts were made on the sensor element and connected to a Keithley multimeter for the resistance measurement. The gas sensing activity was tested at the different operating temperatures in the dynamic system [25], where the sample temperature was controlled with an accuracy of \(\pm\) 1 \(\degree\)C. Air with controlled rate was used as a carrier gas; using a gas tight syringe a known amount of hydrocarbon gas was injected to get required ppm per air level concentration. The sensitivity of the film was calculated as the ratio of change in the conductance to the original conductance. \(s = \Delta\sigma/\sigma_0\) [21].

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns for the (a) pure tin oxide and (b) ruthenated tin oxide films are shown in Fig. 1. The pure tin oxide film has very poor crystalline nature, the very low intensity peaks of 112 and 210 are observed, while the ruthenated tin oxide film exhibits distinct crystalline pattern, supporting our initial finding [25,26] wherein, we reported that the ruthenium probably acts as a nucleating agent promoting low temperature crystallization. The XRD pattern were indexed on the basis of

![Fig. 1. XRD of (a) pure tin oxide and (b) ruthenium incorporated tin oxide thin film fired at 400 °C.](image-url)
tetragonal structure with lattice parameters $a = 4.702$ Å and $c = 3.549$ Å. The grain size calculated from the Scherer formula for the ruthenium incorporated tin oxide thin film is between 17 and 25 nm, which implies formation of a higher surface area thus probably leading to an enhanced sensitivity in the thin film.

3.2. Scanning electron microscopy

Fig. 2 shows the SEM micrographs of pure and ruthenated tin oxide heated at 400 °C in air. The pure tin oxide does not show formation of distinct grains while ruthenium incorporated tin oxide shows distinct grains with size ranging between 50 and 300 nm. The white regions in Fig. 2a are the agglomerated tin oxide as confirmed from EDAX analysis, which may be attributed to the non-uniform distribution of the sol on the substrate. It supports the role of ruthenium species as a nucleating agent for the formation of grains causing the increase in the surface area, which is one of the important factors for the enhancement of sensitivity.

3.3. Gas sensing characteristics

Fig. 3 shows variation in sensitivity for 1000 ppm per air hydrocarbon with the operating temperatures for different weight percentage of ruthenium in the tin oxide matrix. It is observed that the sensitivity increases with temperature, attains a maximum at 300 °C followed by the decrease with further increase in the temperature. It is evident from the figure that the composition containing 0.17 wt.% of ruthenium in tin oxide exhibits highest ($s = 672$) sensitivity towards hydrocarbon. The inset in Fig. 3 shows the dependence of sensitivity on the amount of ruthenium incorporated in the tin oxide matrix. The sensitivity towards 1000 ppm per air hydrocarbon at 300 °C increases sharply when the amount of ruthenium is 0.17 wt.%, which rapidly decreases with the further increase in the amount of
The enhanced sensitivity is attributed to the amount and distribution of ruthenium oxide in the tin oxide matrix. The lower ruthenium concentration causes discontinuity in the distribution, leading to lower sensitivity, while too high concentration leads to the continuous distribution of ruthenium resulting into the lower initial resistance and thereby apparently lower sensitivity values. Moreover, the presence of ruthenium oxide initiates the grain growth and crystallization at the lower firing temperature, it also increases the sites for the adsorption of oxygen. When the hydrocarbon gas, which has reducing nature, is adsorbs on the surface, gets oxidized due to the presence of adsorbed oxygen and releases the electrons in the tin oxide matrix [24]. At the optimum operating temperatures the adsorbed species decompose by getting themselves oxidized, releasing electrons for the conduction in the tin oxide matrix, thus sharply increasing the conductivity. The desorbed species in turn make the oxygen vacancy sites as active centers so that the virgin state is regenerated. The response time for the samples observed was $\sim 15$ s with a recovery time of less than 20 min.

Fig. 4 shows the sensitivity variation with gas concentration. It is found that the sensor exhibits sensing at as low as 50 ppm per air level concentration of hydrocarbon, having a linear increase up to the 1000 ppm per air with saturation at 1200 ppm per air.

As hydrocarbon gas is a highly flammable gas, the sensor should be highly selective and hence the material was tested for the sensitivity towards other commonly interfering gases. Fig. 5 shows a histogram indicating the selectivity of pure and ruthenated tin oxide film (0.17 wt.%) to 1000 ppm per air of various gases. Ruthenium incorporated tin oxide exhibits high selectivity to hydrocarbon, the sensitivity being 672 as compared to 16 for pure tin oxide prepared at similar conditions. Although it shows some sensitivity towards kerosene and alcohol vapors, the gases such as $\text{H}_2$, CO, $\text{NH}_3$, $\text{H}_2\text{S}$, diesel and petrol vapor exhibits negligible sensitivity. The adsorption configurations of the gas molecules and their fragmentation reactions on the ruthenium sites are probably responsible for the high sensitivity and selectivity [24].

4. Conclusion

In conclusion, we have developed a ruthenium incorporated tin oxide thin film sensor element for the selective detection of hydrocarbon gas using a simple spin coating method. It has been observed that ruthenium imparts a considerable degree of specificity and sensitivity. The low temperature of preparation by making use of ruthenium as a sensitizer and as an agent promoting low temperature crystallization has enhanced the selectivity of pure and ruthenated tin oxide film (0.17 wt.%) to 1000 ppm per air of various gases.
the sensing performance remarkably. Moreover, the electronic interaction between metallic additives and semiconductor oxide based gas sensor may be the probable reason for the enhancement of sensitivity towards hydrocarbon.

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References